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In re Application of Ivette Principe

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For: Multiple Layer Cloth for Casino, Gaming and Billiard Tables and Method Therefor

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents  
Washington, D.C. 20231

Sir:

As a means of complying with the duty of disclosure set forth in 37 C.F.R. §1.56, applicant, through the undersigned attorney, files this Information Disclosure Statement pursuant to 37 C.F.R. §1.97.

Patent No.	Inventor	Issue Date
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*[Handwritten signature]*

*9/10/01*

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Respectfully submitted,

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Source: All Sources : Patent Law : Patents : U.S. Patents : Utility Patents **i**  
 Terms: "phosph! fluorocarbon" (Edit Search)

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6,194,497

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Anti-static resin composition containing fluorinated phosphonium sulfonates

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**SEARCH-FLD:** 562#35; 524#165, 912; 522#15, 25, 31, 49, 76

**REF-CITED:**

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**PRIM-EXMR:** Hoke, Veronica P.

**CORE TERMS:** phosphonium, anti-static, resin, sulfonate, thermoplastic, carbon, polycarbonate, atom, polymer, composition, blend, hydrocarbon, fluorinated, aromatic, sulfonic, molded, formula, acid, surfactant, polyphenylene, transparent, ether, fluorocarbon, antistatic, molding, polyester, integer, n.d, polyetherimide, resistivity

#### ABST:

An anti-static thermoplastic resin composition of 90-99.95 weight % of a thermoplastic resin and correspondingly 10 to 0.05 weight % of a halogenated carbon sulfonic acid salt of a polysubstituted phosphonium compound such as a fluorinated phosphonium sulfonate and wherein the thermoplastic resin is either an aromatic polycarbonate, polyetherimide, polyester, polyphenylene ether, polyphenylene ether/styrene polymer blend, polyamide, polyketone, acrylonitrile-butadiene-styrene, blends thereof and blends thereof with other materials. Preferably the thermoplastic resin is a transparent aromatic polycarbonate.

**NO-OF-CLAIMS:** 25

**EXMPL-CLAIM:** 1, 6, 7

**NO-OF-FIGURES:** 0

**NO-DRWNG-PP:** 0

#### SUM:

#### FIELD OF THE INVENTION

This invention is related to an anti-static resin composition particularly transparent resins compositions comprising a thermoplastic polymer and a halogenated carbon sulfonic acid salt of a polysubstituted phosphonium compound and to a halogenated carbon sulfonic acid salt of a polysubstituted phosphonium compound.

#### BACKGROUND OF THE INVENTION

Many polymers or blends of polymers are relatively non-conductive. As such, this can result in a static charge build-up during processing and use of the polymer. The charged polymer molded parts can attract dust, which are small particles, and can thus interfere with a smooth surface appearance. The attracted particles to the surface of a molded article may also cause a decrease in the transparency of the article. In addition, the electrostatic charge can be a serious obstacle in the production process of such polymers. In the past, electrically conductive agents such as carbon and metallic particles or surfactants were used in various attempts to reduce electrostatic charges of synthetic macromolecular materials by mixing them internally together or by coating the material with an agent. These methods employing

electrically conductive agents are not generally feasible for many reasons such as the large amount of agents which must be usually used, the difficulty in adding them to the material, the difficulty in obtaining a transparent product or retention of mechanical and rheological properties, if that is the case, and the high cost of such conductive agents. Thus, these agents can be used only in limited situations.

Anti-static agents are materials which are added to polymers to reduce their tendency to acquire an electrostatic charge, or when a charge is present, these anti-static agents the dissipation of such a charge. The anti-static agents are usually hydrophilic or ionic in nature. When present on the surface of polymeric materials, they facilitate the transfer of electrons and thus eliminate the build up of a static charge. Anti-static agents have been applied in two ways. One method uses external anti-static agents that are applied by spraying the surface or dipping of the polymeric material. The second method uses internal anti-static agents, which are added to the polymer before processing. It is necessary for anti-static agents applied in this manner that they are thermally stable and able to migrate to the surface during processing.

Since there are many anti-static agents having surfactants as their main constituent, appropriate ones may be selected therefrom according to the situation. In fact, many of the types to be internally added have been considered and tried. When used as an internally-applied anti-static agent, however, anionic surfactants are difficult to handle because they are inferior in compatibility and uniform dispersibility and tend to decompose or deteriorate when heated. Cationic surfactants containing quarternary nitrogen in their molecules and amphoteric surfactants, on the other hand, can be used only in limited situations because they are extremely poor in heat resistance, although their anti-static characteristics are good. As for non-ionic surfactants, they are relatively superior to the aforementioned ionic surfactants regarding compatibility with synthetic macromolecular materials, but tend to be weak in anti-static characteristics and their effects disappear with time at normal or high temperatures. Moreover, because of the limited thermal stability of these non-ionic anti-static agents, their use with engineering thermoplastic resins, such as aromatic polycarbonates, is also limited due to the temperatures at which such resins are processed. Thus, these types of surfactants adversely affect the optical properties of aromatic polycarbonates. Although metal salts of organic sulfonic acids have been reported, especially as internally applied anti-static agents for polycarbonates and polyester resins which are molded at high temperatures, they are not sufficient in compatibility with resins or heat resistance one adverse consequence of insufficient compatibility is that transparency characteristics of certain macromolecular materials such as polycarbonates are lost with such anti-static agents. There has also been a report of using phosphonium salts or organic sulfonic acids having halogen substituent as a flame retardant (U.S. Pat. No. 4,093,589), but they are not to be expected to serve as anti-static agents as well.

Another patent discloses reducing the static charge on polycarbonate resins. This is U.S. Pat. No. 4,943,380, which discloses an anti-static composition containing 90-99.9 weight % of polycarbonate and 0.1-10 weight % of a heat resistant phosphonium sulfonate having the general formula:

where R is a straight or branched chain alkyl group having from 1 to 18 carbon atoms; R<1>, R<2> and R<3> are the same, each being an aliphatic hydrocarbon with 1-18 carbon atoms or an aromatic hydrocarbon group; and R<4> is a hydrogen group with 1-18 carbon atoms. The corresponding cationic surfactants containing quarternary nitrogen in their molecules can only be used in limited situations, because they are extremely poor in heat resistance although their anti-static characteristics are good (U.S. Pat. No. 5,468,973).

#### SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an anti-static resin composition

comprising such polymers as polycarbonate, polyetherimide, polyester, polyphenylene ether/polystyrene blends, polyamides, polyketones, acrylonitrile-butadiene-styrene (ABS) or blends of these polymers or blends thereof with other materials or polymers, and a heat resistant anti-static material with which the aforementioned problems of conventional agents can be eliminated.

It is another object of this invention to provide a new anti-static agent which can be internally added to a synthetic resin preferably having transparent characteristics in the molded state without adversely affecting the transparency and mechanical properties of the molded article. However, this invention is not limited to transparent thermoplastics since anti-static requirements are also applicable to pigmented or translucent molded thermoplastic polymer articles.

#### DETAILED DESCRIPTION OF THE INVENTION

Briefly, it has been discovered, according to the present invention, that relatively small quantities of certain heat resistant substituted phosphonium salts of medium and short chain halogenated fluorocarbon sulfonic acids of about 0.05-10 wt %, preferably about 0.2-1.5 wt %, and more particularly about 0.5-1.5 wt %, can be used as internal anti-static agents in polycarbonate, polyetherimide, polyester, polyphenylene ether/polystyrene blends, polyamides, polyketones, ABS or blends of these polymer resins of about 90-99.95 wt %, preferably about 98.5-99.8 wt % and more particularly about 98.5-99.5 wt %, the weight % based on the total weight of polymer and additive. In general, the substituted phosphonium salts of the medium and short chain sulfonic acids have the general formula:

wherein X is independently selected from halogen or hydrogen provided that at least one (1) X is halogen; n, m and p are integers from 0 to 12; and Y is zero or a heterocyclic atom, other than carbon, of an atomic ring and is either nitrogen, oxygen, sulfur, selenium, phosphorus, arsenic, and the like; R<1>, R<2>, and R<3> are the same, each having an aliphatic hydrocarbon radical with 1-8 carbon atoms or an aromatic hydrocarbon radical of 6-12 carbon atoms and R<4> is a hydrocarbon radical with 1-18 carbon atoms. The halogens may be independently selected from bromine, chlorine, fluorine and iodine. Preferably, the halogen is fluorine.

The phosphonium sulfonate is preferably fluorinated phosphonium sulfonate and is composed of a fluorocarbon containing an organic sulfonate anion and an organic phosphonium cation. Examples of such organic sulfonate anions include perfluoro methane sulfonate, perfluoro butane sulfonate, perfluoro hexane sulfonate, perfluoro heptane sulfonate and perfluoro octane sulfonate. Examples of the aforementioned phosphonium cation include aliphatic phosphonium such as tetramethyl phosphonium, tetraethyl phosphonium, tetrabutyl phosphonium, triethylmethyl phosphonium, tributylmethyl phosphonium, tributylethyl phosphonium, trioctylmethyl phosphonium, trimethylbutyl phosphonium, trimethyloctyl phosphonium, trimethylauryl phosphonium, trimethylstearyl phosphonium, triethyloctyl phosphonium and aromatic phosphoniums such as tetraphenyl phosphonium, triphenylmethyl phosphonium, triphenylbenzyl phosphonium, tributylbenzyl phosphonium.

The fluorinated phosphonium sulfonate of the present invention can be obtained by any combination of any of these organic sulfonate anions and organic cations but this invention is not limited by the examples given above. Fluorinated phosphonium sulfonate may be produced in a very pure form by mixing the corresponding sulfonic acid and the quarternary phosphonium hydroxide in a solvent mixture followed by evaporation of the solvent mixture. Tetrabutyl phosphonium perfluoro butane sulfonate, for example, can be produced with a yield of about 95% by placing 98.6 g. of perfluoro butane sulfonic acid, 200 ml. of a 40 wt. solution of tetrabutyl phosphonium hydroxide and a 500 ml of a solvent mixture in a flask, stirring the mixture for one hour at room temperature, isolating phosphonium sulfonate which separates as an oily layer, washing it with 100 ml of water, followed by evaporation of



the solvents using a vacuum pump.

As stated the preferred phosphonium sulfonate employed herein is a fluorinated phosphonium sulfonate having the general formula:

wherein F is fluorine; n is an integer of from 1-12, S is sulfur; R<1>, R<2> and R<3> are the same, each having an aliphatic hydrocarbon radical of 1-8 carbon atoms or an aromatic hydrocarbon radical of 6-12 carbon atoms and R<4> is a hydrocarbon radical of 1-18 carbon atoms. Anti-static compositions comprising fluorinated phosphonium sulfonate shown by formula (3) having the principle component thereof can be used in many different ways to make use of their anti-static and compatibility characteristics and heat resistance in providing such anti-static characteristics to polycarbonate, polyetherimide, polyester, polyphenylene ether/polystyrene blends, polyamides, polyketones, ABS or blends of these polymers. The **phosphonium fluorocarbon** sulfonate salts to this invention are low melting semi-solid materials, and as such, they can be handled as a molten liquid. Some embodiments in the present invention are solid crystalline materials at room temperature (15-25 [degrees] C.) and are easy to weigh, handle, and add to the polycarbonate, polyetherimide, polyester, polyphenylene ether/polystyrene blends, polyamides, polyketones, ABS or blends of these polymers.

A common way to practice this method is to add the agent directly and to mix it at the time of polymer production or fabrication. It can be processed by conventional means, including extrusion, injection, moulding, compression moulding or casting. The quantity of the **phosphonium fluorocarbon** sulfonate salt added to polycarbonate, polyetherimide, polyester, polyphenylene ether/polystyrene blends, polyamides, polyketones, ABS or blends of these polymers is an amount effective to reduce or eliminate a static charge and can be varied over a range. It has been found that if too little of the anti-static substituted **phosphonium fluorocarbon** sulfonate salt is added to the resin, there still may be a tendency for static charge to build up on the article made of the resin. If the loadings of the anti-static additive become too high, the addition of these quantities is uneconomical, and at some level it may begin adversely to affect other properties of the resin. For example, in order to obtain a favorable result by such an internal application method in transparent polycarbonate grades, it is preferable to add an agent of the present invention at the rate of 0.1-1.5 wt % with respect to the molding composition and it is even more preferable to do so at the rate of 0.4-0.8 wt %. Antistats of the present invention are more strongly resistant against heat and can be added in lower quantities than the conventional ionic surfactants, e.g. phosphonium alkyl sulfonates, and the resin compositions have good transparency and mechanical properties.

#### DETAILED DESCRIPTION OF THE EXAMPLES

This invention can be further described by means of the following Examples. It should be understood, however, that this invention shall in no way be restricted by these Examples. In the Examples where comments are in terms of percent, they are percent by weight.

The following two test procedures were employed to analyze samples for anti-static behavior. These were the Dust Attraction test, static charge measurements and the surface resistivity by static charge measurement.

##### Dust Attraction Test

Dust attraction in transparent polycarbonate articles was developed. In this procedure, several color plaques are put in an exicator which is saturated with an in situ prepared NH<4>Cl dust for 60 minutes. The dust chamber is equilibrated for 1 hour before the samples are inserted. After 1 hour, the samples are removed and pictures of the color plaques together with the reference material are made using a projector lamp as a light

source. The plaques are visually analyzed for appearance against a polycarbonate reference plaque containing no anti-static agent.

#### Surface Resistivity

Surface resistivity measurements were made at 55 [degrees] C. because at room temperature resistivity values have values in the range of  $10^{17}$ - $10^{18}$  Ohm, in which range accurate results are difficult to obtain. Therefore, at a temperature of 55 [degrees] C., resistivity values have values in the range of  $10^{13}$ - $10^{14}$  Ohm.

In addition to the above tests, the following tests were also conducted:

*	*
Yellowness Index (YI)	- determined in
*	accordance with
*	ASTM 1925-63T.
Transparency	- determined in
*	accordance with
*	ASTM D-1003.
Haze	- determined in
*	accordance with
*	ASTM 1925 63T and
*	ASTM D-1003.
Melt Volume Rate	- determined in
*	accordance with
*	ASTM - 1238.
*	*

#### DETDESC:

##### EXAMPLE 1

This Example describes the preparation of a fluorinated phosphonium sulfonate of this invention.

Potassium perfluorobutylsulfonate was used as the starting material. The potassium ( $K^{+}$  ion) was first exchanged for a  $H^{+}$  ion using an ion exchange column (Rohm & Haas, Amberjet 1200 H). A second step employed in this procedure was an acid-base reaction using a fluorocarbon tail sulfonic acid and tetra butyl phosphonium hydroxide resulting in a high yield and high purity fluorinated phosphonium sulfonate. The reaction is as follows:

tetrabutylphosphonium nonafluoro-1-butanesulfonate

##### EXAMPLE 2

This Example describes the preparation of a fluorinated phosphonium sulfonate of this invention.

Potassium nona-fluoro-ethoxyethyl sulfonate was used as the starting material. The potassium ( $K^{+}$  ion) was first exchanged for a  $H^{+}$  ion using an ion-exchange column (Rohm & Haas, Amberjet 1200 H). A second step employed in the procedure was an acid-base reaction using a fluorocarbon tail sulfonic acid and tetra butyl phosphonium hydroxide

resulting in a high yield and high purity fluorinated phosphonium sulfonate.

The compound obtained had the following formula:

#### EXAMPLE 3

This example describes the preparation of a fluorinated phosphonium sulfonate of this invention.

Zonyl-TBS (DuPont), which is a mixture of different fluorocarbon containing sulfonic acids and fluorocarbon containing ammonium sulfonates was used as the starting material. The ammonium ( $\text{NH}_4^+$ ) was first exchanged for an  $\text{H}^+$  ion using an ion-exchange column (Rohm & Haas, Amberjet 1200 H). A second step employed in the procedure was an acid base reaction using the mixture of fluorocarbon tail containing sulfonic acids and tetra butyl phosphonium hydroxide. The compound mixture obtained consisted of the following components wherein  $y$  is an integer of 1-9.

#### EXAMPLE 4

The anti-static properties of the fluorinated phosphonium sulfonate of Example 1 above was determined by first melt blending with anti-static agent a transparent aromatic polycarbonate resin having an intrinsic viscosity of about 0.46 deciliters per gram (dl/g) as measured in methylene chloride at 20 [degrees] C. In a twin screw extruder at a temperature of about 285 [degrees] C., extruded through a die orifice into strands which were quenched in water and then pelletized. The pellets were dried at about 125 [degrees] C. for about 2 hours. The dried pellets were injection molded into plaques of about 10 cm. square by about 2.5 mm. thick at an injection molding temperature of about 285 [degrees] C. using a single screw injection molding machine. Obviously, the temperature profile over the injection molding barrel was varied to an ultimate of about 285 [degrees] C. In this Example, the barrel composition set forth in TABLE 1 below was prepared under the same conditions as set forth above with the polycarbonate content varied with respect to the concentration of the anti-static agent present in each formulation. Each formulation also contained the same quantity of mold release agent, UV absorber, stabilizers, antioxidant and dye, the total of which was about 0.8 wt % of the polycarbonate employed. The results obtained were as follows:

TABLE 1						
Anti-Static Concentration (%)	Surface		Appearance		MVR	
	Resistivity	Transparency	Yellowness	Index	Haze	(1.2 kg./ 300 [degrees] C. cm <sup>3</sup> /10 min.
	(10 <sup>14</sup> Ohm at 55 [degrees] C.	(%)	(%)			
0	16.6	89.6	1.35	0.8	12.1	
0.2	6.13	89.4	1.30	0.9	12.4	
0.4	7.63	89.5	1.40	1.0	12.0	
0.5	7.95	89.6	1.50	0.8	11.9	
0.6	1.74	89.5	1.60	0.7	12.1	
0.8	0.26	89.7	1.45	0.8	12.3	
1.0	0.06	89.9	1.50	0.50	12.8	
1.5	0.004	89.0	1.70	0.65	13.6	

The results clearly show the excellent anti-static properties Of the composition Of this invention as shown by the results of surface resistivity and transparency without affecting transparency or color.

#### EXAMPLE 5

The formulations Of Example 4 were molded under abusive molding conditions i.e. the molding temperature of Example 4 + 20 [degrees] C. and a cooling time of 120 seconds compared to normal cooling time in Example 4 of 20 seconds. The results obtained were as follows:

Anti-Static Concentration (%)	Surface Resistivity (10<14> Ohm at (55 [degrees] C.)	Appearance		
		Transparency (%)	Yellowness	
			Index	Haze
0	14.8	89.5	1.50	0.8
0.2	18.8	89.4	1.40	0.85
0.4	11.6	89.5	1.70	1.0
0.5	0.85	89.7	1.70	0.75
0.6	0.33	89.6	1.75	0.85
0.8	0.015	89.7	1.50	0.7
1.0	n.d.	n.d.	n.d.	n.d.
1.5	n.d.	n.d.	n.d.	n.d.

n[Footnotes]

n.d. - not determined

The results of injection molding of the same samples at different levels using abusive conditions (Temp. + 20 [degrees] C. and cooling time = 120 sec instead of 20 sec) are set forth in TABLE 2. Comparison of the results in TABLES 1 and 2 shows that if abusive molding conditions are used, the anti-static additive concentration in order to obtain anti-static polycarbonate is slightly reduced at loadings higher than 0.5%. This is a further indication of the improved surface seeking abilities of the anti-static additive of this invention at even higher processing temperatures. This was also confirmed for parts molded at abusive temperatures ( + 20 [degrees] C.) with the normal cycle time (t = 20 sec). For samples molded using normal and abusive molding with a cycle time of 20 sec using loadings of 0.6% anti-static concentration, the surface resistivity decreased from 1.74 (TABLE 1) to 0.33 (TABLE 2) respectively. These results clearly show the effect of the molding conditions of the surface resistivity behavior and that the surface seeking ability of the anti-static additive is temperature and cycle time dependent.

## EXAMPLE 6

Example 4 was repeated except that the anti-static material employed was EPA-202, a phosphonium sulfonate of the prior art obtained from Takemoto Oil and Fat Co., LTD. The composition of EPA-202 has the following formula and is an anti-static composition of U.S. Pat. No. 4,943,380:

The results obtained were as follows:

Anti-Static Concentration (%)	Surface Resistivity (10 <sup>14</sup> Ohm at 55 [degrees] C.		Appearance Transparency (%)		MVR (1.2 kg./ 300 [degrees] C. cm <sup>3</sup> /10 min.	
			Yellowness Index Haze			
0	*	6.47	*	*	*	*
0.5		6.81	89.6	1.35	0.8	12.07
1.5		1.85	87.9	2.70	2.10	16.97
2.0		0.30	89.1	1.85	1.55	23.00
1.5<(a)>		0.45	89.4	2.05	1.15	26.71
	*		88.6	5.80	0.6	23.00
	*		*	*	*	*
	*		*	*	*	*

n[Footnotes]

<(a)>abusive molding conditions as used in Example 5 above.

It should be noted that the anti-static properties of the anti-static agent of this invention (tetrabutylphosphonium nona-fluoro-1-butanesulfonate Example 1) has better anti-static properties at significantly lower concentration than the anti-static property of the prior art phosphonium sulfonate EPA-202. The lower the surface resistivity the better is the anti-static property of the additive. At 2.0% concentration of the prior art additive, the resistivity is equivalent to just 0.8% concentration of the inventive anti-static additive. Also, it is noted that the EPA-202 is a viscous yellow oil which increases the Yellowness Index while the anti-static additive, Example 1, is a white solid thus facilitating better dispersion of a powder than a viscous oil.

In addition, it is further noted that the melt flow of the composition of the invention is essentially unaffected as determined by MVR. Even at a concentration of 1.5% (TABLE 1) the MVR is only slightly greater than a composition with no additive. In TABLE 3, at a concentration of 1.5% of the prior art anti-static agent, the MVR is almost doubled compared to no additive. This demonstrates that the prior art additive acts as a plastisizer which has a significant negative effect on mechanical properties, particularly aromatic polycarbonate resins.

## EXAMPLE 7

A high flow aromatic polycarbonate resin, having an intrinsic viscosity of about 0.42 deciliters per gram as measured in methylene chloride at 20 [degrees] C., was melt blended and

injection molded under the same conditions as employed in Example 4 except that compact disc (CD) blanks were molded.

Three compositions and sets of CD's (10 per composition) were prepared as described above with the polycarbonate content varied with respect to the concentration of the anti-static agent present in the formulation. Each formulation contained the same quantity of mold release agent and stabilizer.

The sample CD blanks were then evaluated for transparency, color and static charge. The static charge was measured directly after molding on each CD blank from employing a calibrated field hand held meter by SIMCO [r] . The results obtained were as follows:

TABLE	*	*	*		
4	*	*	*		
	*	*	*		
		Antistatic	*		
		concentration		Static Charge	Appearance
		(%)		(Volts)	Transparency      Coloring
	*		*	*	
		0		1400	good      none
		0.3		800	good      none
		0.5		400	good      none
	*		*	*	

The results clearly show that in very high flow grades excellent antistatic properties are obtained without affecting transparency and color.

The formulation containing 0.5% antistatic additive showed no dust attraction in the Dust Attraction Test. The addition of 0.3% antistatic agent showed a large improvement compared to the reference with no anti-static additives.

#### EXAMPLE 8

The antistatic properties of the fluorinated phosphonium sulfonate of Examples 2 and 3 (Formulas 5 and 6) above were determined by first melt blending with anti-static agent, a transparent aromatic polycarbonate resin having an intrinsic viscosity of about 0.46 deciliters per gram (dl/gm) as measured in methylene chloride at 20 [degrees] C., in a twin screw extruder at a temperature of about 285 [degrees] C., extruded through a die orifice into strands which were quenched in water and then pelletized. The pellets were dried at about 125 [degrees] C. for about 2 hours. The dried pellets were injection molded into plaques of about 10 cm. square by about 2.5 mm. thick at an injection molding temperature of about 285 [degrees] C. using a single screw injection molding machine. Obviously, the temperature profile over the injection molding barrel was varied to an ultimate of about 285 [degrees] C. In this Example, the barrel temperature varied from about 20 [degrees] C. to about 285 [degrees] C. Each composition set forth in TABLE 5 below was prepared under the same conditions as set forth above with the polycarbonate content varied with respect to the concentration of the anti-static agent present in each formulation. Each formulation also contained the same quantity of mold release agent, UV absorber, stabilizers, antioxidant and dye, the total of which was about 0.8 wt % of the polycarbonate employed. The results obtained were as follows:

TABLE 5

\*

\*

Anti Static Agent	Concentration Wt. %)	Surface Resistivity	Appearance	
		(10<14> Ohm at 55 [degrees] C.)	Transparency (%)	Yellowness Index Haze
Control	0	16.6	89.6	1.35 0.8
Example 2	0.5	8.90	89.1	1.35 1.0
Example 2	1.0	0.21	89.8	1.40 0.9
Example 3	0.5	7.74	89.2	1.45 1.1
Example 3	1.0	0.12	89.7	1.30 1.4

As seen from the Examples, the results clearly show a lower surface resistivity of the molded plaques with the anti-static composition of this invention at lower additive loadings compared to prior art EPA-202 described in Example 6. Furthermore, with EPA-202, severe yellowing occurred using abusive molding conditions and this is not observed for the newly synthesized anti-static compositions of this invention. Also noted is that EPA-202 appears to be a plasticizer for polycarbonate as shown by the increase in MVR values while essentially no difference in flow is observed for the fluorinated phosphonium sulfonates of this invention.

In the present invention, it is to be understood by those skilled in the art that various changes may be made in the particular embodiments described above without departing from the spirit and scope of the invention as defined in the appended claims.

#### CLAIMS:

What is claimed is:

**[\*1]** 1. A molded article comprising a thermoplastic resin composition having enhanced antistatic properties made by the process of adding an effective amount of an antistatic agent to a thermoplastic resin, and mixing together the agent and the thermoplastic resin at the time of polymer production or fabrication of the molded article by molding, wherein the antistatic agent has the following formula:

wherein X is independently selected from the group consisting of bromine, chlorine, fluorine, iodine and hydrogen, provided that at least one X is selected from the group consisting of bromine, chlorine, fluorine and iodine; n and m are integers from 0 to 12; when p is an integer from 1-12, Y is zero or is selected from the group consisting of nitrogen, oxygen, sulfur, selenium, phosphorus and arsenic, and when p is 0, Y is selected from the group consisting of nitrogen, oxygen, sulfur, selenium, phosphorus and arsenic; R<1>, R<2> R<3> are the same, and are selected from the group consisting of an aliphatic hydrocarbon radical of 1-8 carbon atoms and an aromatic hydrocarbon radical of 6-12 carbon atoms; and R<4> is a hydrocarbon radical of 1-18 carbon atoms.

**[\*2]** 2. The method of claim 1, wherein the thermoplastic resin is selected from the group consisting of aromatic polycarbonates, polyetherimides, polyesters, polyphenylene ethers, polyphenylene ether/styrene polymer blends, polyamides, polyketones, acrylonitrile-butadiene-styrenes, and blends thereof.

**[\*3]** 3. The method of claim 1 wherein the thermoplastic resin composition comprises 90-99.95 weight % of the thermoplastic resin and correspondingly 10-0.05 weight % of the anti-

static agent based on the weight of the thermoplastic resin and additive.

**[\*4]** 4. The method of claim 1 wherein the thermoplastic resin composition comprises about 98.5-99.8 wt % of the thermoplastic resin and about 0.2-1.5 wt % of the anti-static agent.

**[\*5]** 5. The method of claim 1 wherein the thermoplastic resin composition comprises about 98.5-99.5 wt % and about 0.5-1.5 wt % of the anti-static agent.

**[\*6]** 6. The method of claim 1 wherein fluorinated-carbon sulfonic acid salt of the polysubstituted phosphonium compound is a fluorinated phosphonium sulfonate compound of the following formula:

wherein y is an integer of from 1 to 9, R<1>, R<2>, and R<3> are the same and each are selected from the group consisting essentially of an aliphatic hydrocarbon radical of 1-8 carbon atoms and an aromatic hydrocarbon radical of 6-12 carbon atoms, and R<4> is a hydrocarbon radical of 1-18 carbon atoms.

**[\*7]** 7. The method of claim 6 wherein the fluorinated phosphonium sulfonate has the following formula:

**[\*8]** 8. The method of claim 6 wherein the thermoplastic resin is selected from the group consisting of aromatic polycarbonates, polyetherimides, polyesters, polyphenylene ethers, polyphenylene ether/styrene polymer blends, polyamides, polyketones, acrylonitrile-butadiene-styrenes, and blends thereof.

**[\*9]** 9. The method of claim 8 wherein the thermoplastic resin is a transparent aromatic polycarbonate.

**[\*10]** 10. The method of claim 3 wherein X is fluorine.

**[\*11]** 11. The method of claim 10 wherein n is 3 and R<1>, R<2>, R<3> and R<4> are each alkyl radicals of C<4> carbon atoms, and Y and m are zero.

**[\*12]** 12. The method of claim 1 in which the article is transparent.

**[\*13]** 13. The method of claim 12 in which the article is a compact disc blank.

**[\*14]** 14. The method of claim 1 in which the article is translucent.

**[\*15]** 15. The method of claim 12 in which the article is pigmented.

**[\*16]** 16. A molded article comprising a thermoplastic resin composition having enhanced antistatic properties made by the process of adding an effective amount of an antistatic agent to a thermoplastic resin, and mixing together the agent and the thermoplastic resin at the time of polymer production or fabrication of the molded article by molding, wherein the antistatic agent has the following formula:

wherein X is independently selected from the group consisting of bromine, chlorine, fluorine, iodine and hydrogen, provided that at least one X is selected from the group consisting of bromine, chlorine, fluorine and iodine; n and m are integers from 0 to 12; when p is an integer from 1-12, Y is zero or is selected from the group consisting of nitrogen, oxygen, sulfur, selenium, phosphorus and arsenic, and when p is 0, Y is selected from the group consisting of nitrogen, oxygen, sulfur, selenium, phosphorus and arsenic; R<1>, R<2> R<3> are the same, and are selected from the group consisting of an aliphatic hydrocarbon radical of 1-8 carbon atoms and an aromatic hydrocarbon radical of 6-12 carbon atoms; and



R<4> is a hydrocarbon radical of 1-18 carbon atoms.

**[\*17]** 17. The article of claim 16 which is transparent.

**[\*18]** 18. The article of claim 17 which is a compact disc blank.

**[\*19]** 19. The article of claim 16 which is translucent.

**[\*20]** 20. The article of claim 16 which is pigmented.

**[\*21]** 21. The method of claim 16 wherein the thermoplastic resin composition comprises 90-99.95 weight % of the thermoplastic resin and correspondingly 10-0.05 weight % of the antistatic agent based on the weight of the thermoplastic resin and additive.


**[\*22]** 22. The method of claim 16 wherein the thermoplastic resin composition comprises about 98.5-99.8 weight % of the thermoplastic resin and corresponding by about 0.2-1.5 weight % of the antistatic agent.

**[\*23]** 23. The method of claim 16 wherein the thermoplastic resin composition comprises about 98.5-99.5 weight % and corresponding by about 0.5-1.5 weight % of the antistatic agent.

**[\*24]** 24. The composition of claim 16 wherein the antistatic agent is a fluorinated phosphonium sulfonate compound of the following formula:

wherein y is an integer of from 1 to 9, R<1>, R<2>, and R<3> are the same and each are selected from the group consisting essentially of an aliphatic hydrocarbon radical of 1-8 carbon atoms and an aromatic hydrocarbon radical of 6-12 carbon atoms, and R<4> is a hydrocarbon radical of 1-18 carbon atoms.

**[\*25]** 25. The composition of claim 16 wherein the fluorinated phosphonium sulfonate has the following formula:

Source: [All Sources](#) : [Patent Law](#) : [Patents](#) : [U.S. Patents](#) : [Utility Patents](#) 

Terms: "phosph! fluorocarbon" ([Edit Search](#))

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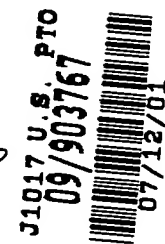
Terms: abst (phosphorus w/4 fluorocarbon) (Edit Search)

Pat. No. 5833874, \*

5,833,874

Nov. 10, 1998

*only PATENT FOUND*



Fire extinguishing gels and methods of preparation and use thereof

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**US-CL:** 252#8; 252#3; 252#8.05; 169#11; 169#44; 169#46

**CL:** 252;169

**SEARCH-FLD:** 252#8, 3, 8.05; 169#11, 44, 46

**REF-CITED:**

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<u>4,652,383</u>	3/1987	* Tarpley, Jr. et al.	252#8
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**CORE TERMS:** composition, particle, polyoxyethylene, gel, surfactant, powder, ammonium, dry, micron, extinguisher, fire-extinguishing, polyphosphate, ether, acid, atom, sec, flame, salt, gelling, nitrogen, compound, gas, cylinder, formula, lbs, proportion, sodium, gms, phosphate, extinguishing

**ABST:**

Fire-extinguishing compositions of low ozone depletion potential comprise dry particles of fire-extinguishing agents dispersed in a gel of liquified volatile perfluorocarbons, chlorofluorocarbons or hydrofluorocarbons. The dry particles are compatibilized with the carrier gel by the presence of a surfactant system composed of a non-ionic surfactant, a film forming **fluorocarbon** surfactant and a **phosphorus** containing antiflocculent.

**NO-OF-CLAIMS:** 22

**EXMPL-CLAIM:** 1

**NO-OF-FIGURES:** 0

**NO-DRWNG-PP:** 0

**SUM:**

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to fire-extinguishing gel compositions useful in extinguishing Class A, Class B, Class C and Class D fires.

2. Brief Description of the Related Art

The literature is replete with descriptions of fire-extinguishing compositions. Included in such compositions are gelled compositions comprising dry solid chemicals for extinguishing flames and inhibiting oxidation (for example sodium and potassium bicarbonate) and vaporizing organic liquids like brominated hydrocarbons. The latter compounds also extinguish flames very effectively. The mechanism by which brominated hydrocarbons extinguish flames is two-fold. The primary mechanism involves the termination of free radical reactions that sustain combustion and a secondary mechanism is heat abstraction associated with a high vapor heat capacity and a high heat of vaporization.

A study by the Purdue Research Foundation (Final Report on Fire Extinguishing Agents, Purdue Research Foundation and Dept. of Chemistry with Army Engineers Research and Development Labs., Fort Belvoir, 1950) established at that time as a standard for effectiveness in flame extinguishing, the brominated hydrocarbon bromotrifluoromethane (HALON 1301; the "HALON" system of nomenclature was devised by the Army Corps. of Engineers to identify halogenated hydrocarbons by the numbers of carbon, fluorine, chlorine, bromine and iodine atoms). The study also established HALON 1301 as the least toxic of the brominated hydrocarbon organic liquids for flame extinguishing. The Purdue Research Foundation Report led to the extensive use of HALON 1301 and HALON 1211 (bromochlorodifluoromethane) bromofluorocarbons as volatile, vaporizing organic liquids in flame extinguishing. Unfortunately, the bromofluorocarbons have the potential for destroying ozone in the upper stratosphere, when released into the environment. This impact on the environment has been of great concern.

Subsequently, some 90 countries participated in a treaty to phase out use of the ozone-destroying bromofluorocarbons such as those widely used in commercial applications,

including as fire extinguishers. Thus, there is a need for products to replace especially HALON 1301 and HALON 1211. Such products must have acceptable low toxicity, environmental acceptance and comparative performance on a weight/weight or volume/volume basis.

A number of perfluorocarbons, chlorofluorocarbons (CFC) and hydrofluorocarbons (HFC) by themselves have been identified as potentially useful to extinguish fires in flooding applications, and being free of bromine content or low in chlorine content, have little or no ozone depletion potential (ODP). Representative of these perfluorocarbons, chlorofluorocarbons and hydrofluorocarbons are 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoroethane, perfluorocyclopropane, perfluoropropane, perfluorocyclobutane and the like; see U.S. Pat. No. 5,135,054, which is incorporated herein by reference thereto. The chlorofluorocarbon compounds are also referred to by the "CFC" system of nomenclature, the hydrofluorocarbons by the "HFC" system. Under these systems, the first digit represents the number of carbon atoms minus one (and is omitted if zero); the second digit represents the number of hydrogen atoms plus one; and the third digit represents the number of fluorine atoms. For example, HFC-125 represents pentafluoroethane.

However, the low ozone depletion potential substitutes described above and in U.S. Pat. No. 5,135,054 have not, in general, been as effective as the ozone-destroying bromofluorocarbons, particularly in regard to their use in forming stable gels as carriers for dry powder chemicals, especially in streaming applications (where the agent is applied from extinguishers which direct a stream of the agent on the fire site). Streaming compositions, particularly those which are carried in non-aqueous gels, tend to clog in the dispenser nozzle and are difficult to maintain in homogeneous dispersions before dispensing.

Although it was known that tetrafluoroethane was a flame inhibitor (see U.S. Pat. No. 4,459,213, Col. 2, line 61) its use in flame extinction has not been exploited. This is understandable, when one considers that the gas has a high potential for toxicity, being decomposed by high temperatures (open flames, glowing metal surfaces) to form the hazardous compounds hydrofluoric acid and carbonyl fluoride. It is also incompatible with alkaline earth metals, powdered aluminum, zinc, beryllium and the like. Furthermore, initial tests of 1,1,1,2-tetrafluoroethane indicated that as a flame inhibitor the gas per se was no more effective than bromotrifluoromethane; see the U.S. Pat. No. 5,135,054.

We have now discovered that 1,1,1,2-tetrafluoroethane and other hydrofluorocarbons, iodofluorocarbons and chlorofluorocarbons of low ODP can be compounded with certain dry chemicals, in a substantially non-aqueous gel to enhance their covering of exposed flaming flammable surfaces to enhance its effectiveness. The compositions of the invention are hybrids, i.e., gelled formulations of dry powder agents delivered in liquified hydrofluorocarbons and chlorofluorocarbons. These compositions extinguish flame so rapidly that decomposition of the gas component to undesired toxic products of burning is minimal. In tests, sampling for decomposition products showed no significant formation of HF or COF<sub>2</sub>.

The compositions of the invention are stable dispersions of low ozone depletion potential and are highly effective in extinguishing Class B and C fires. Some are also useful to extinguish Class A and Class D fires as defined by the National Board of Fire Underwriters. They are effective when applied in both "streaming" and "flooding" applications.

#### SUMMARY OF THE INVENTION

The invention comprises a substantially non-aqueous, flame-extinguishing gel composition of low ozone depletion potential, which comprises;

a plurality of particles of a dry powder fire-extinguishing agent, dispersed in a gel, comprised of:

a liquefied fire-extinguishing gas of low ozone depletion potential;

a hydrophilic, non-ionic surfactant;

a film-forming fluorocarbon surfactant; and

an anti-flocculent proportion of a phosphorus containing antiflocculent.

The invention also comprises the use of the compositions of the invention to extinguish fires.

The term "low ozone depletion potential" (ODP) as used herein means a value of less than about 0.5 as determined by the method of Fisher et al., Nature, Vol. 344, pages 508-512 (Apr. 5, 1990).

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

Dry powder fire-extinguishing agents are represented by ammonium sulfate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium borate, potassium borate, sodium borate (borax), sodium sulfate, sodium phosphate, sodium polyphosphate, sodium chloride, potassium chloride, ammonium bromide, mono- and diammonium phosphate and the like. Preferred dry powder fire-extinguishing agents are solid forms of the ammonium and sodium salts of polyphosphoric acids (ammonium or sodium polyphosphate). The ammonium polyphosphate solid particles are preferred dry chemical agents for practice of the present invention, since they are inherently polyanions which repel each other, avoiding self-agglomeration. Advantageously, the ammonium polyphosphate solid particles employed in the preferred compositions and method of the invention are prepared by methods well-known in the art, for example, by heat treating phosphates such as urea phosphate with a combined ammoniating and condensing agent such as urea or melamine. Further details of the commercial preparation of ammonium polyphosphates may be found in U.S. Pat. Nos. 3,755,163 and 3,775,315, both incorporated herein by reference thereto. These ammonium polyphosphates are compounds containing a P-O-P type linkage, having the general formula:



wherein n is an integer of at least about 17. The physical characteristics of these ammonium polyphosphates and the various processes for preparing them are described, for example, in U.S. Pat. No. 3,397,035 dated Aug. 13, 1968. Water solubility of the polyphosphate is increased as the degree of ammoniation is lowered and as the polymer chain length is decreased.

Especially good results are obtained in the present invention with the use of ammonium polyphosphates of formula (I) given above, having an n value between 1000 and 5000, preferably between 1000 and 3000.

The preferred ammonium polyphosphates to be used in accordance with the present invention are solids and have an apparent density between about 0.4 and 0.9 kg/liter, as compared with other powdered fire-extinguishing agents having an apparent density between about 0.4 and 0.45 kg/liter. A phosphorus content of 31.5 +/- 0.5% by weight and a water-soluble content of less than 10% measured in a 10% strength aqueous dispersion at a temperature of 25o C. is advantageous.

The particles are advantageously provided in the form of free-flowing, finely divided particles, (crystals or granules), the average particle size being a maximum of 500 microns, advantageously within the range of from about 0.05 to 500 microns, preferably 1 to 100 microns, most preferably less than about 50 microns. Especially good results are obtained in flooding applications using particle sizes of 1 to 12 microns (average).

The particles of dry powder fire-extinguishing agents are uniformly and homogeneously dispersed in the volatile liquid gel. Any of the known perfluorocarbon, chlorofluorocarbon and hydrofluorocarbon fire-extinguishing gases of low ozone depletion potential may be used as the gellable liquid in compounding the compositions of the invention. Representative of those gases are HFC-23, HFC-31, HFC-32, HFC-124, HFC-125, HFC-134, HFC-134a, HFC-218, HFC-227ea, HFC-318, HFC-236fa and the like (see U.S. Pat. No. 5,185,094 incorporated by reference).

The proportion of volatile liquid in the preferred gel compositions of the invention may range from about 30 to about 70 percent by weight of the total gel composition, preferably 40 to 60 percent. The lower the proportion of volatile liquid, the lower is the potential for toxic gases released by fire exposure. Gelling agents for use in gelling non-aqueous dispersions of dry powdered fire-extinguishing agents in organic liquids are well known and include for example pyrogenic silica (such as the commercially available CAB-O-SIL H5 marketed by G. L. Cabot, Inc., Boston, Mass.; pyrogenic alumina (such as Alan C); carboxymethyl cellulose, carrageenin, polycarboxylated vinyl polymers such as carboxypolymethylene and those described in U.S. Pat. No. 4,652,383, incorporated herein by reference thereto, guar gum and the like. A preferred gelling agent is fumed silica-alumina (Coke Registered TM -84; DeGussa, Inc. Teterboro, N.J.).

The gelling agents are present in the preferred compositions of the present invention in an amount sufficient to effect gelation of the liquid ingredients. Advantageously, the proportion of gelling agent used is within the range of from 0.05 to 10 percent by weight of the volatile liquid. Gelation is preferably the formation of a thixotrope, having a yield stress of at least about 200 dynes per cm<sup>2</sup>. Unexpectedly, we found that when the dry particle ingredients have an average size of from 1 to about 12 microns, the amount of gelling agent required to effect gelation of the liquid ingredient is dramatically reduced, i.e.; requiring about one-tenth the amount needed for compositions containing dry particles of larger particle sizes.

The gelling causes the gas and dry particles to "hang together". As a result, the volatile liquid effectively carries the dry powder ingredients directly to the fire, around corners and through clutter (places where nitrogen gas propelled powder compositions generally cannot be directed).

10mic problem  
The HALON type gases have formed relatively stable gel compositions, without the use of stabilizing additives. This is not the case when substituting hydrofluorocarbons and chlorofluorocarbons for HALONS, in gel compositions. Due to the differences in polarity and solvent power, of gelled hydrofluorocarbons or chlorofluorocarbons, the suspended dry particles have a tendency to agglomerate in the gelled, liquefied volatile gas. Agglomeration of the particles can clog the dispensing nozzle, resulting in an ineffective application. To overcome this tendency for particle agglomeration, we have of necessity incorporated into the gel compositions of the invention a surfactant and deflocculant system comprised of a plurality of particular and specified surfactants. The surfactant system stabilizes the gel composition and prevents agglomeration and separation of the solid particles from the dispersion.

The term "surfactant" as used herein is a contraction of "surface-active agent" and is a broadly descriptive term used to describe a chemical compound which is (1) soluble in at least one phase of a system, (2) has an amphipathic structure, (3) the molecules of which form oriented monolayers at phase interfaces, (4) exhibits an equilibrium concentration as a

solute at a phase interface, greater than its concentration in the bulk of the solution, (5) forms micelles when the concentration as a solute in solution, exceeds a characteristic limiting value and (6) exhibits some combination of the functional properties of detergency, foaming, wetting, emulsifying, solubilizing and dispersing. The surfactants for combination in the gel carriers of the present invention are chosen for their primary functions as polarization neutralizers, lubricants and wetting agents. In the gelled carrier described herein, the formulation with dry fire extinguisher powders is stable for optimal periods of time, to enhance dispensing of the fire extinguishant and to promote rapid extinguishing of flames.

In a gelled composition of the invention, a non-ionic hydrophilic surfactant is included to assist in stabilizing the dispersion of the dry particles in the gel.

As examples of hydrophilic, non-ionic surfactant, there may be mentioned polyoxyethylene sorbitan fatty acid ester such as polyoxyethylene sorbitan monooleate, polyoxyethylene sorbitan monostearate, or polyoxyethylene sorbitan tetraoleate; polyoxyethylene sorbitol fatty acid ester such as polyoxyethylene sorbitol monolaurate, polyoxyethylene sorbitol monooleate, polyoxyethylene sorbitol pentaoleate, or polyoxyethylene sorbitol monostearate; polyoxyethylene glycerol fatty acid ester such as polyoxyethylene glycerol monostearate, polyoxyethylene glycerol monoisostearate, or polyoxyethylene glycerol triisostearate; polyoxyethylene fatty acid ester such as polyoxyethylene monooleate, polyoxyethylene distearate, polyoxyethylene monodioleate, or ethylene glycol distearate; polyoxyethylene alkyl ether such as polyoxyethylene lauryl ether, polyoxyethylene oleyl ether, polyoxyethylene stearyl ether, polyoxyethylene behenyl ether, polyoxyethylene 2-octyl dodecyl ether, or polyoxyethylene cholestanol ether; polyoxyethylene alkyl phenyl ether such as polyoxyethylene octyl phenyl ether, polyoxyethylene nonyl phenyl ether, or polyoxyethylene dinonyl phenyl ether; Pluronic-type surface-active agent such as Pluronic; polyoxyethylene polyoxypropylene alkyl ether such as polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene polyoxypropylene 2-decyl tetradecyl ether, polyoxyethylene polyoxypropylene monobutyl ether, polyoxyethylene polyoxypropylene hydrogenated lanolin, or polyoxyethylene polyoxypropylene glycerol ether; tetrapolyoxyethylene tetrapolyoxypropylene -ethylene diamine condensate such as Tetronic; polyoxyethylene castor oil or hardened, castor oil derivatives such as polyoxyethylene castor oil, polyoxyethylene hardened castor oil monoisostearate, polyoxyethylene hardened castor oil triisostearate, polyoxyethylene hardened castor oil monopyroglutamic acid monoisostearic acid diester, or polyoxyethylene hardened castor oil maleic acid; polyoxyethylene bees wax laurin derivatives such as polyoxyethylene sorbitol bees wax; alkanol amide such as coconut oil fatty acid diethanol amide, lauric acid monoethanol amide, or fatty acid isopropanol amide; polyoxyethylalkyl amine, polyoxyethylene fatty acid amide, sucrose fatty acid ester, polyoxyethylene nonyl phenyl formamide condensate, alkyl ethoxy dimethylamine oxide, trioyleyl phosphate, and the like.

The non-ionic surfactant is advantageously present in a weight proportion of from about 0.5 to 10 percent by weight of the total weight of gelled composition of the invention, preferably less than 5 percent.

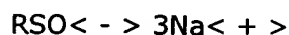
It is also advantageous, when the dry particles to be dispersed in the gel composition are polar materials, to counter the polarity of the particles. This can be accomplished by adding to the compositions a depolarizing proportion of an anionic surfactant. Representative of anionic surfactants are surfactant compounds which contain an organic hydrophobic group containing from about 8 to 26 carbon atoms and preferably from about 10 to 22 carbon atoms in their molecular structure; and at least one water-solubilizing group selected from the group consisting of sulfonate, sulfate and carboxylate so as to form a water-soluble surfactant.

Examples of anionic surfactants include soaps, such as, the water-soluble salts (e.g., the sodium, potassium, ammonium and alkanol-ammonium salts) of higher fatty acids containing

from about 8 to 20 carbon atoms.

Other anionic surfactants are the alkane sulfonates including long chain alkane sulfonates and long chain hydroxyalkane sulfonates. Also the sulfated ethoxylated higher fatty alcohols of the formula  $RO(C_2H_4O)_mSO_3M$ , wherein R is a fatty alkyl of from 10 to 22 carbon atoms, m is from 2 to 6 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in R) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanolamino, or higher alkyl benzene sulfonate wherein the higher alkyls of 10 to 15 carbon atoms are present. The proportion of ethylene oxide in the polyethoxylated higher alkanol sulfate is preferably 2 to 5 moles of ethylene oxide groups per mole of anionic surfactant, with three moles being most preferred, especially when the higher alkanol is of 11 to 15 carbon atoms.

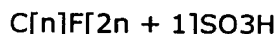
Another class of preferred anionic surfactant found useful as a component of the compositions of the invention are the sulfonates of formula:



wherein R is a hydrocarbyl group. Representative of such sulfonates are sodium xylene sulfonate, sodium lauryl sulfate and the like.

A depolarizing amount of anionic surfactant is generally from about 0.5 to about 10.0 percent by weight of the total weight of the gel composition of the invention.

Minor amounts (0.001 to 0.5 parts by weight of the total gel composition) of film-forming surfactants such as the fluorocarbons described in U.S. Pat. Nos. 2,937,098 and 3,163,547 (incorporated herein by reference thereto) are also used in the gel compositions of the invention. These are generally provided in relatively small proportions as emulsions in alcohols such as isopropyl alcohol. Particularly useful in the present invention are the anionic or cationic perfluorinated surfactants, such as the perfluorinated sulphonic acids having the general formula:



where  $C_n$  denotes an aliphatic chain, straight or branched containing from 5 to 20 carbon atoms. The acids are toxic and because of this suitable salts such as the alkali metal salts, for example, the sodium or potassium salts are preferably used. An example of a particularly suitable perfluorinated surfactant is that having the formula  $C_8F_{17}SO_3NH_4$ . Perfluorinated surfactants are commercially available from the 3M Company, Minneapolis, Minn. The perhalogenated surfactant is usually available in commerce in a mixed aqueous /organic solvent system and may be utilized in that form in the practice of this invention. A preferred emulsion product is Zonyl FSN, a fluorocarbon surfactant composition containing 1.0% active ingredient; E. I. DuPont DeNemours and Company, Wilmington, Del. When added to the compositions of the invention, the solvent is dispersed and the surfactant precipitates as a film, forming on the solid particles dispersed in the gel carrier.

Critical to the compositions of the invention which include the dry powders described above, is the presence of a phosphorus containing antiflocculent, which is compatible with fire-extinguishing agents. Representative Of antiflocculents containing phosphorus are compounds such as the phosphoric acid ester salts like alkylphosphates, alkyl ether phosphates, and alkylallyl ether phosphates.

Preferred phosphorus containing antiflocculents are the acidic phosphorus-containing compounds, for example, the water-soluble di- or polyphosphonic or di- or polyphosphinic acid esters or water-soluble salts thereof. Representative of the phosphonic or phosphinic acid esters or salts thereof are those of the general formulae (II) to (VI) as follows:



$$Y_2-(X)[n(II)]$$

$$[Y(X)[n]]_3N(III)$$

$$[[Y(X)[n]]_2N]_2(X)[n(IV)]$$

$$[[Y(X)[n]]_2N(X)[n]]P(V)$$

$$[[Y(X)[n]]_2N(X)[n]]_3N(VI)$$

where P represents a phosphonic or phosphinic acid radical or water-soluble salt (preferably ammonium) of such a radical;

N represents a nitrogen atom,

X represents the methylene or substituted methylene radical  $-CR_2$  or, where  $(X[n])$  is directly bonded to 2 nitrogen atoms and n is greater than 1, two adjacent X groups may represent a part of a cycloalkyl, preferably a cyclohexyl, group,

n represents a whole number from 1 to 5,

R represents  $-H$ ,  $-OH$  or  $-(CH_2)_2H$  or part of a shared cycloalkyl group.

Compounds according to the above general formulae (II)-(VI) are widely available commercially usually as solutions, e.g. of 50% to 75% by weight, in water, for example from the Monsanto Company, St. Louis Mo., under the Trade Name Dequest Registered TM. Although these compounds are provided in aqueous solution, because limited proportions are used, the overall contribution of water to the total composition of the invention is negligible and the total gel composition is substantially "non-aqueous" in nature.

Specific preferred compounds are:

Formula (II)

1-hydroxyethylidene 1,1-diphosphonic acid (Dequest Registered TM 2010) and the tetra sodium salt thereof (Dequest Registered TM 2016)

Formula (III)

aminotrimethylene phosphonic acid (Dequest Registered TM 2000)

Formula (IV)

ethylenediaminetetra (methylene phosphonic acid) ammonium salt (Dequest Registered TM 2042) and the hexamethylenediamine variant of the last compound (Dequest Registered TM 2052)

Formula (V)

diethylenetriaminepenta (methylene phosphonic acid) (Dequest Registered TM 2060).

Similar products are also available under the Trade Names "Mykon" P060 and "Briquest" APPA 60A.

The phosphonic or phosphinic acid salts are employed in an anti-flocculent proportion, which

is generally within the range of from 0.5 to 10 percent by weight of the total gel composition of the invention.

Those skilled in the art will appreciate that ammonium polyphosphate, described above as a preferred dry powder fire-extinguishing agent ingredient for the compositions of the invention are also, inherently, antiflocculents and that function is exploited in the present invention when they are employed as the dry powder fire-extinguishing agent. In other words, when the compositions of the invention include at least 0.5 to 10.0 percent by weight of ammonium polyphosphate particles, the need for an antiflocculent is satisfied.

The preferred compositions of the invention may be containerized within containers having the structural strength for withstanding the superatmospheric pressures developed during storage and ambient use temperatures. Generally, these pressures will be within the range of from about 15 to 250 PSIG at room temperatures. The container loading is facilitated by cooling the compositions of the invention below their critical vapor pressures, during loading.

The container compositions of the invention may also be overpressured to facilitate discharge, with non-flammable gases such as nitrogen, carbon dioxide, helium, argon and like inert gases, using conventional techniques. To facilitate ease of use of the compositions of the invention, the compositions are contained in a flame [or fire] extinguishing system. Such systems may comprise containment means for holding under superatmospheric pressure the compositions and valve means on the containment means for release of the contained compositions from the containment means onto the flame [or fire] to be extinguished. Advantageously, the system is fitted with sensor means for detecting a fire and automatically operating the valve means.

The following examples and preparations describe the manner and process of making and using the invention and set forth the best mode contemplated by the inventors of carrying out the invention but are not to be construed as limiting the invention.

#### GEL STABILITY STUDIES

A plurality of pressure-resistant, clear glass vessels were provided, each fitted with an aerosol valve (Bespak Company) and a dip tube for containing a series of fire-extinguishing compositions. The compositions were loaded into the vessels under pressure and allowed to stand for at least 36 hours. At the end of this period of time, the pressurized contents of the vessels were discharged by use of an actuator. Weights of the vessels were taken before release of the contents and after release to calculate the percentage of the composition which discharged. The greater the percentage of expulsion, the greater is the stability and effectiveness of the dispersion as an indicator of lack of separation. The composition ingredients and the percentages expelled are given below.

#### DETDESC:

##### EXAMPLE 1

A composition of the invention is prepared by dispersing 100.4 gms of monoammonium phosphate (MAP) having an average particle size of 30 microns in 120.3 gms of 1,1,1,2-tetrafluoroethane (HFC-134a; gelled with 2.0 gm of fumed silica/alumina (Coke Registered TM 84, DeGussa, Inc., Teterboro, N.J., and containing 1.0 gms of polyoxyethylene sorbitol (Tween Registered TM 80, ICI, Wilmington, Del.) 0.1 gms of Zonyl Registered TM FSN fluorosurfactant, supra., and 2.0 gms of an anti-flocculent (Dequest Registered TM 2016; Monsanto Company, St. Louis, Mo.). Upon actuation, 88.4% of the particles are expelled from the container without flow interruption.

**EXAMPLE 1-B (Control)**

For purposes of comparison, a control composition was prepared as described in Example 1 above, but without addition of the polyoxyethylene sorbitol. Upon actuation, the gel exhibited poor flow and only 72.9% of particle expulsion occurred.

**EXAMPLE 1-C (Control)**

For purposes of comparison, a control composition was prepared as described in Example 1, supra., but without addition of the Zonyl Registered TM FSN fluorosurfactant. Upon actuation, 70.3% expulsion of particles occurred with poor flow.

**EXAMPLE 1-D (Control)**

For purposes of comparison, a control composition was prepared as described in Example 1, supra., but without addition of the Dequest Registered TM 2016. Upon actuation, poor flow occurred, with clumping. The expulsion accounted for 74.7 percent of the particles.

Repeating the general procedure of Example 1, supra., but replacing the HFC 134a as used therein with an equal weight of one of the following volatile gases,

trifluoromethane (HFC-23)

pentafluoroethane (HFC-125)

heptafluoropropane (HFC-227ea)

1,1,1,3,3,3-hexafluoropropane (HFC-236fa)

perfluoropropane (FC-218)

perfluorobutane (FC-3-1-10) or

trifluoroiodomethane (FIC-1311)

there is obtained a composition of the invention useful to extinguish fires and is equal in flow and stability to the HFC 134a-containing formulation of Example 1, supra.

**EXAMPLE 2**

Repeating the procedure of Example 1, supra., but replacing the monoammonium phosphate as used therein with an equal weight of potassium bicarbonate (average particle size 30 micron), a gel composition was obtained which upon actuation released 88.4 percent of the particles with good flow from the container.

**EXAMPLE 2-B (CONTROL)**

The procedure of Example 2, supra., was repeated except that the polyoxyethylene sorbitol was not added. Upon actuation, 65% of the particles were expelled, with poor flow.

### EXAMPLE 2-C (Control)

The procedure of Example 2, *supra*, was repeated, except that the Dequest Registered TM 2016 as used therein was omitted. The expulsion upon actuation accounted for 77.7 percent of the particles with poor flow and clumping.

### EXAMPLE 3

Repeating the procedure of Example 1, *supra*., but replacing the monoammonium phosphate as used therein with an equal weight of ammonium polyphosphate (of formula (I), *supra*., Phos-Chek Registered TM P/30; n = 1000 to 3000, Monsanto Company, St. Louis, Mo.) having average particle size of 30 micron and replacing the polyoxyethylene sorbitol as used therein with an equal proportion of ethoxylated/propoxylated C8-C10 alcohols (Antarox BL-240; Rhone-Poulenc, Cranbury, N.J.) and omitting the Dequest Registered TM 2016 as used therein, there is obtained a gel which expels smoothly (92.8% particle expulsion) from the containing vessel.

The product of Examples 1, 2 and 3 are environmentally safe. The ODP of HFC-134a is zero. The atmospheric lifetime is 15.4 years. The 100-yr CO<sub>2</sub> for the global warming potential (GWP) is 1200. The dry chemical component does not affect the atmosphere, other than as a dust. All components are environmentally acceptable for production and use. Since the components do not chemically combine, they separate upon release into their original forms. Therefore, no new chemical compounds are created and there is no environmental impact.

### EXAMPLE 4

The procedure of Example 1, *supra*., was repeated except that the HFC-134a as used therein was replaced with an equal proportion of HFC-125. The gel/particle dispersion obtained is equal in flow and stability to the HFC-134a containing compositions.

### STREAMING AGENT EVALUATION

Small-scale streaming tests were performed with 4-inch high 18 in x 18 in square pans (2.25ft<2> ). The pans were filled with 1-inch of n-heptane floated on water. A steel structure was fabricated to surround the pan and virtually eliminate any effects caused by wind. The structure was 16 ft x 16 ft x 8 ft high. Additionally, a wind curtain was extended 5 feet above the structure to help mitigate effects associated with wind.

An intermediate-scale (32 ft<2> ) pool fire test was also performed. This pool was a circular steel pit with 2 inches of Jet A fuel floating on 10 inches of water. There was a 3 inch "lip" above the fuel surface.

#### Small-Scale Tests

The extinguisher used for the small-scale tests was fabricated from a stainless steel cylinder having a capacity of 1-gallon. The extinguisher had a valve on one end and a hose on the other. The valve, located on the top of the extinguisher, had a quick-disconnect for filling. A nitrogen hose was attached to the same quick-disconnect to provide for a constant nitrogen overpressure during the test. Connected to the end of the hose was a nozzle assembly taken directly from one of the 11/4 Halon 1211 extinguishers. The flexible hose, which was 2.5 feet in length, made it easy to apply the agent with a consistent sweep rate. The agent could also be applied at the desired angle of attack.

The extinguisher was mounted on a pulley system which was designed to support the extinguisher, yet still allow the firefighter the freedom of movement. The firefighter simply rolled the extinguisher along the pulley system into the desired position for the test. The extinguisher could easily be removed from the pulley system between tests and weighed.

#### Intermediate-Scale Fire Extinguisher

An Amerex 20-lb Halon 1211 fire extinguisher was used for the intermediate-scale tests.

Five different sizes of nozzles were used during the small-scale testing. The orifice sizes were as follows: 0.067, 0.076, 0.082, 0.090, and 0.098 inches. The 0.082 and 0.090 nozzles were fabricated by drilling out the center of a 0.067 nozzle to obtain the desired bore.

The test procedures were basically the same as for the small-scale tests. In an effort to keep the technique consistent, the same firefighter was used for all of the tests. The test procedures are summarized below:

1. The extinguisher was weighted empty to establish a tare weight.
2. The extinguisher was filed with the desired amount of powder (APP or MAP) and the gaseous agent (HFC-125 or HFC-134a) the gelling agent and surfactant system and shaken vigorously by hand until the "gelling" of the agent could be felt.
3. The extinguisher was pressurized with nitrogen.
4. The extinguisher was weighted to establish the initial weight of the extinguisher and the agent blend.
5. The extinguisher was attached to the pulley system and the nitrogen overpressure hose was connected to the extinguisher.
6. The fire pan was filled with 3-inches of water and 1-inch of heptane.
7. The fire was ignited and a 60 sec preburn was established.
8. The agent was applied to the fire by squeezing the nozzle fully and producing a sweeping motion across the fire. The agent was initially applied to the front of the pan in an effort to push the fire to the back of the pan until extinguishment was achieved. Every effort was made to keep the agent on the fire and minimize overspray.
9. The time from agent application to extinguishment was recorded with a stopwatch.
10. The extinguisher was weighed to determine the amount of agent dispensed.

The above procedures were also used during the intermediate-scale (32ft<2> ) tests; however, the extinguisher did not have a constant nitrogen overpressure.

#### SMALL-SCALE TEST RESULTS

The compositions of the invention were effective in extinguishing the fires, particularly the APP/HFC-134a blend. The test results are shown in Table 1, below. The APP/134a blend (weight ratio of 45% particles:55% liquid) had a minimum weight to extinguish of 0.30 lb. The extinguishment time was 1.65 sec.

TABLE I

*	Optimum	Ext.	Agent
Agent	Flowrate,	Time,	Used
	(lbs/sec)	(sec)	(lb)
Halon 1211	0.18	1.6	0.28
(Control)			
45% APP/55%134a	0.18	1.6	0.30
45% MAP/55%134a	0.15	3.1	0.45

### Test Summaries

#### Halon 1211 (Control)

Ten tests were performed with Halon 1211 on the 2.25 ft<2 > fires. The fire was easily extinguished in each of these tests. The quickest extinguishment time was 1.6 sec, in which 0.28 lb of agent was consumed. The flowrate was 0.18 lbs/sec.

#### HFC-134a (Control)

Three tests were performed with the HFC-134a. The agent was applied to the 2.25 ft<2 > fire and extinguishment was achieved in one of the tests. It took however, 29 sec, and 4.52 lbs of agent was required. The flowrate was 0.16 lbs/sec. The next test was performed with a much higher flowrate (0.29 lbs/sec.). The agent was extremely ineffective at this flowrate. The agent appeared to blow right through the fire, and was unable to push the fire to the back of the pan. A total of 5.46 lbs. of agent was used in this test. The flowrate was lowered for the next test, down to 0.18 lbs/sec. The agent performed similarly to the first test, but extinguishment was not achieved after 28 sec had elapsed and 5.2 lbs. of agent had been used.

#### 45% APP/55% 134a (Invention)

Nine tests were performed with this blend. The blend appeared to be extremely effective. The fire was extinguished very quickly, and rather easily in the tests. The quickest extinguishment time was 1.65 sec in which 0.30 lb. of agent was consumed. The corresponding flowrate was 0.18 lbs./sec.

#### 45% MAP/55% 134a (Invention)

Six test were performed with this blend. The blend was effective, but not nearly as effective as the APP blend. The quickest extinguishment time was 3.1 seconds in which 0.45 lb. of agent was consumed. The flowrate was 0.15 lbs/sec.

### TOTAL-FLOOD EVALUATION

The fire tests used to evaluate the total flood extinguishment effectiveness of the products included Class 1 wood cribs (1/2 of a 1A crib) and Class B pool fires. The Class B fuel was n-heptane floated on water in various circular pans. Approximately 1/2 in of fuel was floated on 2.5 in of water. The water was required to decrease pan warpage. The circular pan sizes were 1/4 in steel, 8.5-in diameter (0.4 ft<2> , 35 Kw) and 1.33-ft diameter (1.4 ft<2> , 209 Kw) all 4 in deep and corresponding to fire heat release rate to test chamber volume ratios of 1.9 and 11.4 Kw/m<3 > (0.62 and 2.15 ft<2> /1000 ft<3> ), respectively.

The blends tested were based on a percent mass composition. Several discharge cylinders were used. A particular cylinder was chosen based upon the total charge weight and desired cylinder fill ratio. The cylinder was weighed so that a tare weight was obtained prior to filling. The desired weight of the composition for testing was added to the cylinder. The halocarbon liquid agent was added last to the cylinder by weight to the desired mass ratio and then the cylinder was pressurized with nitrogen gas. A total weight was determined. The total weight included the nitrogen overpressure. The cylinder with the powder, the halocarbon agent, gelling agent, surfactant system and nitrogen was then shaken (mixed) until the mixture blended (gelled) together. This gelling effect was noticeable as the cylinder was being shaken. The cylinder was then attached to the discharge system. After a one minute pre-discharge the agent was discharged into the chamber.

After the discharge was completed the cylinder post weight was measured to determine the amount of powder left in the cylinder (all of the gaseous agent was discharged).

From previous testing done, a composition of 45 percent powder to 55 percent halocarbon agent by mass was first tried. The first test conducted was of the 45 percent APP (7 micron average particle size) powder and 55 percent HFC-134a by mass to determine if the agent would flow through the piping system. The doors on the test chamber were left open and the agent was observed being expelled through the agent discharge pipe network. The fire was 35 kW and was extinguished prior to the end of the discharge. The test was considered to be a success. The agent weight was felt to be excessive since the fire was extinguished during the agent discharge and the test chamber doors were open.

The next step in the testing was to find the lower bounds, by mass, needed to extinguish the fire. The powder mass in the blend was lowered; however, the percent composition was kept at 45 percent by mass composition. The test chamber doors were kept closed throughout the rest of the testing. Tell tale fires consisting of 2 inch diameter cups 4 inches tall with 2 in heptane were placed in all eight corners, top and bottom of the test chamber to determine the agent mixing characteristics in the test chamber. The total agent weight was lowered to approximately two pounds (powder plus halocarbon agent).

#### Fire Extinguishing Results

There were several total-flood tests performed with the compositions of the invention. Table II, below summarizes the results.

The fire extinguishing effectiveness was equal to or better than the existing Halons in total flooding and streaming applications.

TABLE II

	*	*	*	*	*	Actual	*	
	*	HFC-	*	Weight	Actual	Total	Calc.	
	APP	134a	*	Agent	Powder	Agent	Gaseous	Center
Test	Weight	Weight	Discharge	Used,	Conc.	Conc	Agent	Fire Out,
No.	lbs.	lbs.	Time, sec	lbs.	g/m<3>	g/m<3>	Conc. %	(sec)
1	4.50	5.50	4.5	9.20	80	229	4.0	yes
2	6.10	9.00	6.0	13.40	109	333	6.5	8
3	5.50	8.00	6.5	13.57	135	337	5.8	5.5
4	5.50	8.00	*	*	*	*	*	6
5	5.00	8.60	*	*	*	*	*	4
6	4.50	6.50	6.0	12.46	96	310	6.2	4
7	4.00	5.80	*	*	*	*	*	6

8	3.50	5.30	*	*	*	*	*	7
9	3.00	4.50	*	*	*	*	*	7
10	3.50	5.25	6.0	8.20	67	204	3.8	7
11	4.00	6.00	7.2	10.00	92	248	3.8	7
12	4.00	6.00	5.0	8.40	45	209	4.3	7

It was previously appreciated that very fine particles of fire-extinguishing powders, that is, particles in the micron size, are highly effective in extinguishing fires; see U.S. Pat. No. 4,234,432. However, such small particle sizes cause difficulties in terms of the discharge of the powders from dissemination apparatus. The finely divided powder particles tend to agglomerate and form masses, which clog the nozzles, valves and other parts of the apparatus, especially after sitting for a period of time. The patentee in U.S. Pat. No. 4,234,432 approached the problem by providing the particles in a bimodal particle size distribution, wherein the larger powder particles had an average approximate maximum dimension of about 4 to about 10 times greater than the average approximate maximum dimension of the smaller powder particles. This is a manufacturing problem, requiring the obtaining and mixing of the bimodal particles. We have found that employing the surfactant system described above and as employed to prepare the gelled compositions of the present invention, less than 10 micron sized particles (average diameter) may be used to obtain shelf-stable compositions for effective use in fire extinguishers.

#### EXAMPLE 5

A composition of the invention was prepared following the general procedure of Example 1, *supra.*, mixing the following ingredients.

100 gms of ammonium polyphosphate (Phos-Chek Registered TM . *supra.*) having an particle size of 7 micron.

125 gms of HFC 134a, *supra.*

0.2 gms of Zonyl Registered TM FSN, *supra.*

1.0 gms of AntaroX Registered TM BL-240, *supra.*

0.5 gms of Coke Registered TM 84, *supra.*, gelling agent.

Upon actuation, 92.7 percent of the particle expelled in a homogeneous, uninterrupted flow.

#### EXAMPLE 6

To evaluate the comparative fire-extinguishing effect of the 30 micron (average) sized particles used in the composition of Example 4, *supra.*, against the 7 micron (average) sized particles used in the composition of Example 5, *supra.* Testing in a flood application was conducted using 1000 ml. of heptane fuel floated on 1000 ml. of water in a 5.5 cubic meter box. On average, 460 gms of the composition of Example 4 (30 micron particles) was required to effect flame extinction, while only 375 gms. of the composition of Example 5 (7 micron particles) was required.



**CLAIMS:** What is claimed is:

**[\*1]** 1. A substantially non-aqueous, flame-extinguishing gel composition of low ozone depletion potential, which comprises;

a plurality of particles of a dry powder fire-extinguishing agent, dispersed in a gel, comprised of:

30 to 70 percent by weight of the total gel composition of a liquefied fire-extinguishing, gas of low ozone depletion potential;

0.5 to 10 percent by weight of the total gel composition of a hydrophilic, non-ionic surfactant;

0.001 to 0.5 parts by weight of the total gel composition of a film-forming fluorocarbon surfactant of the formula:

$C[n]F[2n + 1]SO_3H$  wherein n is from 5 to 20, and the alkali metal salts thereof; and

5 to 10 percent by weight of the total gel composition of a phosphorus-containing antiflocculent.

**[\*2]** 2. The composition of claim 1 wherein the particles are selected from the group consisting of ammonium sulfate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium borate, potassium borate, sodium borate, sodium sulfate, sodium phosphate, sodium polyphosphate, sodium chloride, potassium chloride, ammonium bromide, monoammonium phosphate, diammonium phosphate, and ammonium polyphosphate.

**[\*3]** 3. The composition of claim 1 wherein the particles have maximum average particle sizes of 500 microns.

**[\*4]** 4. The composition of claim 3 wherein the average particle sizes are less than about 50 microns.

**[\*5]** 5. The composition of claim 4 wherein the average particle sizes are about 30 microns.

**[\*6]** 6. The composition of claim 1 wherein the p article size averages 1 to 12 microns.

**[\*7]** 7. The composition of claim 1 wherein the particles are particles of ammonium polyphosphate.

**[\*8]** 8. The composition of claim 7 wherein the ammonium polyphosphate has the general formula:



wherein n is an integer of at least about 17.

**[\*9]** 9. The composition of claim 8 wherein n has a value of between 1000 and 5000.

**[\*10]** 10. The composition of claim 8 wherein n has a value of between about 1000 and 3000.

**[\*11]** 11. The composition of claim 10 wherein the average particle size is about 30

microns.

**[\*12]** 12. The composition of claim 1 wherein the gas is selected from the group consisting of a perfluorocarbon, a chlorofluorocarbon, an iodofluorocarbon and a hydrofluorocarbon.

**[\*13]** 13. The composition of claim 12 wherein the gas is 1,1,1,2,-tetrafluoroethane.

**[\*14]** 14. The composition of claim 12 wherein the gas is pentafluoroethane.

**[\*15]** 15. The composition of claim 12 wherein the gas is trifluoriodomethane.

**[\*16]** 16. The composition of claim 1 wherein the proportion is 40 to 60 percent.

**[\*17]** 17. The composition of claim 1 wherein the gel is formed by a gelling agent selected from the group consisting of pyrogenic silica, pyrogenic alumina, carboxymethyl cellulose, carrageenin, polycarboxylated vinyl polymers and guar gum.

**[\*18]** 18. The composition of claim 17 wherein the gelling agent selected is fumed silica - alumina.

**[\*19]** 19. The composition of claim 1 wherein the phosphorous containing antiflocculent is selected from the group consisting of:

Y<sub>2</sub>-(X)[n(II) ]

[Y(X)[n]]<sub>3</sub>N(III)

[[Y(X)[n]]<sub>2</sub>N(X)[n]]Y(IV)

[[Y(X)[n]]<sub>2</sub>N(X)[n]]Y(V)

and

[[Y(X)[n]]<sub>2</sub>N(X)[n]]<sub>3</sub>N(VI)

where Y represents a phosphonic or phosphinic acid radical or water-soluble salt of such a radical;

N represents a nitrogen atom,

X represents the methylene or substituted, methylene radical -CR<sub>2</sub> or, where (X)[n] is directly bonded to 2 nitrogen atoms and n is greater than 1, two adjacent X groups may represent a part of a cycloalkyl,

n represents a whole number from 1 to 5; and

R represents -H, -OH or -(CH<sub>2</sub>)<sub>2</sub>H.

**[\*20]** 20. The composition of claim 1 wherein the phosphorus containing antiflocculent is ammonium polyphosphate.

**[\*21]** 21. The composition of claim 1 where in the non-ionic surfactant is polyoxyethylene sorbitol.

**[\*22]** 22. The composition of claim 1 which further comprises an anionic surfactant.

Source: [All Sources](#) : [Patent Law](#) : [Patents](#) : [U.S. Patents](#) : [Utility Patents](#) **i**


Terms: **abst (phosphorus w/4 fluorocarbon)** ([Edit Search](#))

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Source: All Sources : Patent Law : Patents : U.S. Patents : Utility Patents Terms: "phosphate ester" w/s fluoropolymer ([Edit Search](#))

Pat. No. 5962129, \*

5,962,129

Oct. 5, 1999

Flame retardant hot melt compositions

**INVENTOR:** Halloran, Kristine D., St. Paul, Minnesota  
Chase, Cheryl Y., White Bear Lake, Minnesota**ASSIGNEE-AT-ISSUE:** H.B Fuller Licensing & Financing, Inc. (02)**APPL-NO:** 3,974**FILED:** Jan. 7, 1998**INT-CL:** [6] B32B 7#12; B01D 50#00**US-CL:** 428#355EN; 428#348; 428#920; 428#921; 55#497; 55#521; 524#487**CL:** 428;55;524**SEARCH-FLD:** 428#348, 355EN, 198, 920, 921; 210#493.1, 493.5; 55#497, 500, 521; 524#487**REF-CITED:**

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**CORE TERMS:** adhesive, composition, wax, filter, resin, flame, melt, smoke, hot, retardant, copolymer, compound, ethylene, viscosity, oxygen, rosin, hydrocarbon, tackifying, polymer, melting point, inorganic, filler, zinc, hydrated, generation, measured, antioxidant, tradename, borate, alumina trihydrate

**ABST:**

The present invention relates to a flame retardant hot melt composition comprising from about 20% to about 60% by weight of the adhesive of at least one copolymer of ethylene, from about 10% to about 50% by weight of the adhesive of a flame retarding hydrated inorganic compound, from about 10% to about 30% by weight of at least one high melting point wax and from about 1% to about 10% by weight of at least one tackifying resin.

**NO-OF-CLAIMS:** 11

**EXMPL-CLAIM:** 1

**NO-OF-FIGURES:** 0

**NO-DRWNG-PP:** 0

**SUM:**

**FIELD OF THE INVENTION**

This invention relates to an ethylene copolymer based flame retardant hot melt adhesive composition.

**BACKGROUND OF THE INVENTION**

Hot melt compositions find use as adhesives, coatings and sealants. These compositions do not, however, have good flame retarding characteristics in and of themselves, making it necessary to add flame retarding compounds which function under heat to yield compositions which are more difficult to ignite. These compounds act under intense heat and high temperatures by absorbing heat, by decomposing to form a nonflammable ash or coating to provide a barrier against heat transfer or by evolving products such as water vapor which retards or stops further propagation of a fire. Flame retardancy is measured by the oxygen index which is a vertical burning test. An oxygen index of 21 indicates that a composition would burn in atmosphere so the oxygen index is generally required to be 23 or higher to have flame retarding characteristics. The smoke generation of these materials must also be acceptably low before they will be approved for use by the Underwriters' Laboratory (UL).

Both organic and inorganic compounds have been used for flame retardancy. Organic flame retardants include chlorinated paraffins, **phosphate esters**, chlorinated alicyclic hydrocarbons, **fluoropolymers**, polyvinyl chloride and a variety of other halogenated organic compounds. Halogenated compounds produce products having poor thermal stability resulting in poor color retention and production of noxious fumes. In U.S. Pat. No. 4,169,082 to Kusterer, Jr. issued Sep. 25, 1979, a chlorinated paraffin wax is used as the flame retardant. Such halogenated compounds have been found to produce too much smoke in the compositions of the present invention. The disadvantages of using halogenated compounds are described in U.S. Pat. No. 5,378,856 to Allen issued Jan. 3, 1995. Usually these compounds are used in conjunction with an inorganic flame retardant such as antimony

oxide.

Inorganic compounds, also referred to as fillers, include antimony oxide, magnesium hydroxide, zinc borate, barium metaborate, alumina trihydrate, zinc oxide, ammonium octamolybdate and magnesium distearate.

Polymeric based hot melt compositions containing flame retardant materials have been used for many purposes including sealing and jacketing of power cables, insulation and jacketing of electrical conductors and coatings for electrical and optical wires wherein the polymeric composition acts as a layer of insulation. The compositions typically used in these areas have a polymeric material and a filler. These types of compositions may be found in U.S. Pat. No. 4,849,135 to Reitz issued Jul. 18, 1989; U.S. Pat. No. 4,948,669 to Rolland issued Aug. 14, 1990; U.S. Pat. Nos. 4,575,184 and 5,059,651 to Ueno issued Mar. 11, 1986 and Oct. 22, 1991, consecutively; U.S. Pat. No. 5,378,856 to Allen issued Jan. 3, 1995 and U.S. Pat. No. 5,482,990 to Jow et al. issued Jan. 9, 1996.

U.S. Pat. No. 5,059,651 to Ueno specifically teaches a flame retardant and smoke suppressed polymeric composition comprising a radiation cured copolymer of ethylene and vinyl acetate containing 50-85% by weight vinyl acetate and a flame retarding and smoke suppressing amount of a filler mixture. These compositions contain uncrosslinked vinyl acetate polymers which gain strength only upon curing. At column 3 lines 37 to 43 it is stated that "a copolymer of ethylene and vinyl acetate containing about 60% by weight of vinyl acetate and having a molecular weight of about 200,000, as admixed with the same weight of a finely divided inorganic filler (aluminum hydroxide), has a tensile strength as low as 0.1 kg/mm<sup>2</sup>, and is of no practical use." Furthermore, these compositions are very high in viscosity and are intended to be used as sheathing for electrical wire.

U.S. Pat. No. 5,317,051 to Harashige et al. issued May 31, 1994 teaches a flame-retardant olefin polymer composition superior in surface whitening prevention having a blend of a resin component consisting principally of an olefin resin and an olefin polymer modified with an unsaturated carboxylic acid or derivative thereof, a flame retardant and a whitening preventing agent. Harashige teaches that these compositions are useful for electric wires, cables, packages, sealing materials, hoses, films, molded products and master batches.

In addition to the above applications, flame retardant compositions are useful in the air filter industry, and in particular are useful for High Efficiency Particulate Air (HEPA) Filters. In this situation, the compositions act as adhesives to adhere the pleats of the filters together. These adhesives are extruded onto the filters and each filter pleat is adhered to the next. The difficulty in using the polymeric compositions described above is that the viscosities of these compositions are too high for use in hot melt application equipment. In order to lower the viscosity of a hot melt adhesive, it is common to replace part of the polymer with lower molecular weight materials such as resin and wax. However, when commonly used proportions of these materials are used, the smoke generation upon burning is unacceptably high. In addition, lowering the polymer content to decrease viscosity can result in decreased filler acceptability and decreased flexibility of the resultant composition.

HEPA filters utilizing a hot melt adhesive as a filter pleating adhesive are discussed in U.S. Pat. No. 4,365,980 to Culbert et al. issued Dec. 28, 1982. Culbert discusses utilizing a hot melt adhesive, "Instant Lok," supplied by National Adhesives, Inc. This hot melt is ethylene vinyl acetate based and is generally used for case and carton sealing. It has greater than 25% tackifying resin, has no flame retardant and is therefore not a flame retardant adhesive. See column 3 lines 63 to 68.

It is an object of the present invention to provide a novel polymeric based flame retardant composition which has a relatively low viscosity, is flexible in a thin bead or film and adheres well to a variety of porous substrates while maintaining a high oxygen index and low smoke

generation.

## SUMMARY OF THE INVENTION

The present invention relates to a flame retardant hot melt composition comprising from about 20% to about 60% by weight of the adhesive of at least one copolymer of ethylene, from about 10% to about 50% by weight of the adhesive of a hydrated inorganic compound, from about 10% to about 30% by weight of at least one high melting point wax and from about 1% to about 10% by weight of at least one tackifying resin.

The present invention further relates to a flame retardant hot melt composition consisting essentially of from about 20% to about 60% by weight of the adhesive of at least one copolymer of ethylene, from about 10% to about 50% by weight of the adhesive of a hydrated inorganic compound and from about 10% to about 30% by weight of at least one high melting point wax.

The resultant composition is characterized as having an oxygen index of greater than about 23 and preferably greater than about 25 and a smoke number preferably less than about 6, more preferably less than about 5 and most preferably less than about 3.

The resultant composition is further characterized as having a viscosity of less than about 30,000 cPs at about 135°C., preferably less than about 25,000 cPs and most preferably less than about 20,000 cPs and Young's Modulus from about 1500 kg/cm<sup>2</sup> to about 10,500 kg/cm<sup>2</sup> and preferably from about 2500 kg/cm<sup>2</sup> to about 6000 kg/cm<sup>2</sup>.

The compositions are useful where flame retardancy is a requirement, specifically in the air filter industry and in particular for High Efficiency Particulate Air (HEPA) filters.

The present invention further relates to a High Efficiency Particulate Air Filter comprising a material effective for filtering airborne contaminants and an adhesive applied to the material wherein the adhesive comprises from about 20% to about 60% by weight of the adhesive of at least one copolymer of ethylene, from about 10% to about 50% by weight of the adhesive of a hydrated inorganic flame retarding compound and from about 10% to about 30% by weight of at least one high melting point wax.

The filter may be pleated prior to or after application of the adhesive to the filter media or filter material.

## DETDISC:

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The copolymers of ethylene useful to the present invention include ethylene n-butyl acrylates, ethylene methyl (meth) acrylates, ethylene ethylacrylates and interpolymers of ethylene with at least one C3 to C20 alpha-olefin. Ethylene n-butyl acrylate copolymers are available from such companies as Elf Atochem North America in Philadelphia, Pa. under the tradename of Lotryl Registered TM, from Exxon Chemical Co. in Houston, Tex. under the tradename of Escorene Registered TM, from Du Pont de Nemours & Co. in Wilmington, Del. under the tradename of Elvaloy Registered TM and from Millennium Petrochemicals in Rolling Meadows, Ill. under the tradename of Enathene Registered TM. Ethylene methyl acrylate copolymers are available from Exxon Chemical Co. under the tradename of Optema Registered TM. Ethylene vinyl acetate copolymers are available from Du Pont under the tradename of Elvax Registered TM and from Millennium Petrochemicals under the tradename of Ultrathene Registered TM to name only a couple. The term "copolymer" in the present sense is simply meant to refer to copolymerization of ethylene and also encompasses the use

of terpolymers.

The interpolymers of ethylene with at least one C3 to C20 alpha -olefin are homogeneous linear or substantially linear polymers further characterized in that each interpolymer has a polydispersity of less than about 2.5. These polymers are available from Exxon Chemical Co. under the tradename of Exact Registered TM, which are ethylene-butene copolymers and under the tradename of Exxpol Registered TM which are ethylene-propylene copolymers. Ethylene/1-Octene copolymers are available from Dow Chemical Co. in Midland, Mich. under the tradenames of Affinity Registered TM, Insite Registered TM and Engage Registered TM.

The polymers preferable for use in the present invention preferably have a melt index greater than about 400 g/10 minutes as measured by ASTM D 1238 and more preferably greater than about 800 g/10 min. The testing conditions used are commonly 190o C. with a 2.16 kg weight. Testing conditions are generally specified by the manufacturers of the polymers and are determined by such things as the molecular weight and melting point of the polymer. Commercially available ethylene copolymers generally have melt indices of no greater than about 5000 g/10 minutes. Ethylene copolymers having higher copolymer contents, such as greater than about 25% copolymer by weight, generally have melt indices of less than about 3000 g/10 minutes and more commonly less than about 2500 g/10 min. The copolymer content is preferably from about 25% to about 45% by weight of the polymer and preferably from about 25% to about 35% by weight of the polymer. Increasing the amount of the copolymer to greater than about 45% by weight results in a polymer that is very soft, lacks sufficient tensile strength and may remain tacky at room temperature. It is surmised that the polarity of these compounds help to better disperse and retain the inorganic fillers. Having copolymer contents ranging from about 25% to about 45% by weight helps increase desired flexibility in the final composition. In a preferred embodiment, an ethylene vinyl acetate copolymer having a vinyl acetate content of about 28% by weight of the polymer and melt index of about 400 g/10 minutes is utilized. In another preferred embodiment, a blend of ethylene vinyl acetate copolymers having a vinyl acetate content of about 28% and having melt indices of 800 and 2500 g/10 min. is used.

The current inventors envision that other polymers could be used in combination with the copolymers of the present invention provided that the desirable characteristics of the final hot melt composition are not altered.

The flame or fire retardant compounds useful to the present invention include hydrated inorganic compounds, or metal hydrates, which function by absorbing heat, evolving water vapor or steam which dilutes combustible gases being generated, producing a nonflammable char barrier between the heat source and the material and also functions as a smoke suppressant. These compounds have the advantage that they do not contain halogens which are noxious and can be quite toxic when released.

Examples of useful flame retardants, also properly referred to as fillers, include alumina trihydrate, magnesium hydroxide, hydrated calcium silicates, hydrated calcium carbonates and basic magnesium carbonates.

Sources of alumina trihydrate flame retardants include Akron Chemical Co. in Akron, Ohio, Aluchem Inc. in Ohio, CSA Chemical in New Jersey, Fiberchem Inc. in Washington, GCA Chemical Corp. in Connecticut, Great Lakes Minerals Co., Specialty Products Division in Michigan, Harwick Chemical Corp. in Ohio, R.J. Marshall Co. in Michigan, New England Resins & Pigments Corp. in Massachusetts, Smith Chemical & Color Co. in New York, Summit Chemical Co. in Ohio and Westport Industries Inc. in Missouri. Sources of magnesium hydroxide (Mg(OH)<sub>2</sub>) include the Polymer Additives Group, a Division of R.J. Marshall Co. in Southfield, Mich. and J.M. Huber Corp. in Norcross, Ga. While the selection of a flame retardant filler is vast, the alumina trihydrate and the magnesium hydroxide are preferably used in the present invention. Alumina trihydrate, which has a greater degree of hydration, is



most preferable to the present invention.

A zinc borate flame retardant filler may optionally be used in the present invention.

The zinc borate is known to act well as a smoke suppressant and is usually used in combination with antimony oxide for flame retardance in PVC, polyolefins, unsaturated polyesters, thermoplastic polyesters, epoxies, nylons, urethane and phenolics. See, for instance, U.S. Pat. No. 4,439,572 to Kindrick issued Mar. 27, 1984; U.S. Pat. No. 4,833,190 to Cella et al. issued May 23, 1989; U.S. Pat. No. 4,921,897 to Danforth et al. issued May 1, 1990 and U.S. Pat. No. 5,298,544 to Goff issued Mar. 29, 1994. U.S. Pat. No. 5,059,651 to Ueno issued Oct. 22, 1991 uses zinc borate in combination with hydroxides or carbonates of di- and tri-valent metals. These optional fillers are useful up to about 40% by weight of the composition, preferably from about 10% to about 20% and most preferably from about 1% to about 10% by weight of the composition. The present inventors have found that while the zinc borate is useful to reducing smoke generation, it is not a necessary component. Alternatives to zinc borate may include barium borate, ammonium fluoroborate, barium metaborate, zinc stearate, ammonium octamolybdate and zinc stannate to mention only a few.

One example of a zinc borate filler useful herein has the formula,  $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ , or in other words, 45% ZnO, 34% B<sub>2</sub>O<sub>3</sub> and 20% water hydration. The H<sub>2</sub>O content is between about 3.3 to 3.7 and the hydrated form is desired, although nonhydrated forms are available. The particle size is usually 2-10 microns and the refractive index about 1.58. This composition may be found under the tradename of Firebrake Registered TM ZB manufactured by U.S. Borax in Valencia, Calif. and marketed by Harwick in Akron, Ohio.

Any of these hydrated fillers can be surface treated with a saturated or unsaturated carboxylic acid having about 8 to about 24 carbon atoms and preferably about 12 to about 18 carbon atoms or a metal salt thereof. Mixtures of these acids and/or salts can be used, if desired. Examples of suitable carboxylic acids are oleic, stearic, palmitic, isostearic and lauric. Examples of metals which can be used to form the salts of these acids are zinc, aluminum, calcium, magnesium and barium. Examples of the resultant salts include magnesium stearate, zinc oleate, calcium palmitate, magnesium oleate and aluminum stearate. The amount of acid or salt can be in the range of about 0.1 to about 5 parts of acid and/or salt per one hundred parts of metal hydrate and is preferably about 0.25 to about 3 parts per one hundred parts of metal hydrate. The surface treatment is described in U.S. Pat. No. 4,255,303. The acid or salt can be merely added to the composition in like amounts rather than using the surface treatment procedure. The surface treatment, while allowing the compounds to more readily mix and disperse with polymers, is not necessary and generally adds more cost to the resultant filler, therefore making it more undesirable where cost is an issue.

The waxes useful herein are those classified as high melting point waxes. These waxes typically having melting points greater than about 80° C. and preferably greater than about 90° C. The waxes generally having melting points no higher than about 120° C. and more typically are less than about 115° C. Useful waxes include synthetic high melting point waxes and high melting point microcrystalline waxes. Synthetic high melting point waxes include high density, low molecular weight polyethylene waxes, by-product polyethylene waxes and Fischer-Tropsch waxes. By-product polyethylene simply refers to the fact that the product is a by-product of a process which is used to obtain another chemical. For instance, waxes may be produced as a by-product of petroleum cracking process. These by-product waxes are also high density, low molecular weight polyethylene. Preferred waxes include Petrolite Registered TM C-4040, Polywax Registered TM 1000, 2000 and 3000, low molecular weight polyethylene waxes available from Petrolite Corp.; Escomer Registered TM H-101, a modified polyethylene wax available from Exxon Chemical Co. in Houston, Tex; Marcus Registered TM 100, 200 and 300, low molecular weight polyethylene waxes available from Marcus Chemical Co., a

Division of H.R.D. Corp. located in Houston, Tex; and Paraflint Registered TM H-1, H-4, and H-8, Fischer-Tropsch waxes available from Sasol-SA/Moore & Munger in Shelton, Conn.

The microcrystalline waxes useful herein are those having about 50% by weight or more cyclo or branched alkanes with a length of between about 30 and 100 carbons. They are generally less crystalline than the high melting point polyethylene waxes, and have melt points of greater than about 80o C. Examples of these waxes include Be Square Registered TM 175 Amber Wax, an 80o C. melt point microcrystalline wax, Be Square Registered TM 185 Amber Wax, an 85o C. melt point microcrystalline wax, and Be Square Registered TM 195 Amber Wax, a 90o C. melt point wax all available from Petrolite Corp. and Petrowax Registered TM 9508 Light, a 90o C. melt point wax available from Petrowax Pa., Inc. located in New York, N.Y.

In preferred embodiments, synthetic high melting point waxes are used. Although the microcrystalline waxes are also very useful, the viscosity of the finished product is generally higher with the microcrystalline waxes.

These high melting point waxes are useful from about 5% to about 30% by weight of the composition and preferably from about 10% to about 30% and more preferably from about 15% to about 25% by weight of the composition.

Other waxes may be used in combination with the high melting point waxes. These include paraffin waxes and lower melting point microcrystalline waxes. The paraffin waxes useful herein are those having a Ring and Ball softening point of about 50o C. to about 80o C. Useful examples include Okerin Registered TM 236TP available from Astor Wax Corporation located in Doraville, Ga., Penreco Registered TM 4913 available from Pennzoil Products Co. in Houston, Tex., R-7152 Paraffin Wax available from Moore & Munger in Shelton, Conn., and Paraffin Wax 1297 available from International Waxes, Ltd in Ontario, Canada. Examples of useful microcrystalline waxes include Victory Registered TM Amber Wax, a 70o C. melt point wax available from Petrolite Corp. located in Tulsa, Okla.; Bareco Registered TM ES-796 Amber Wax, a 70o C. melt point wax available from Bareco in Chicago, Ill. and Okerin Registered TM 177, an 80o C. melt point wax available from Astor Wax Corp. These waxes are useful up to about 20% by weight of the composition and preferably up to about 10% by weight of the composition.

A wax is necessary to the present invention to lower the viscosity without increasing smoke generation. It has been found that utilizing high amounts of tackifying resins to reduce viscosity tends to also increase the smoke generation. The high melting point waxes are preferred to improve heat resistance as measured by peel and shear values.

Chlorinated waxes have been used as flame retardants such as in U.S. Pat. No. 4,948,669 to Rolland issued Aug. 14, 1990. However, these compounds have been found to produce too much smoke when used in the compositions of the present invention. It has also been desirable to users of flame retardants to eliminate the use of halogenated compounds due to the health and safety hazards of using such compounds.

The tackifying resins useful herein include aliphatic, cycloaliphatic and aromatic hydrocarbon resins and modified hydrocarbons; terpenes and modified terpenes; rosins and modified rosins, including rosin esters, and mixtures thereof. One skilled in the art would know that these resins are all available with different levels of saturation or hydrogenation. This is often measured by the bromine number. For instance, the Eastotac Registered TM series of cycloaliphatic hydrocarbon resins from Eastman Chemical Co. in Kingsport, Tenn. are available in the E, R, L and W grades. The E series typically has a bromine number of about 15, while the R, L and W series have bromine numbers of about 5. These resins are also available with different softening points of 100o C., 115o C. and 130o C. Eastotac Registered TM H-142R is also available with a bromine number of about 5 and a softening point of about

140o C. Other useful resins include Escorez Registered TM 5300 and Escorez Registered TM 5400, partially hydrogenated cycloaliphatic petroleum hydrocarbon resins, and Escorez Registered TM 5600, a partially hydrogenated aromatic modified petroleum hydrocarbon all having softening points of about 100o C. and available from Exxon Chemical Company in Houston, Tex.; Wingtack Registered TM Extra which is an aliphatic, aromatic petroleum hydrocarbon resin, Wingtack Registered TM 86, an aromatic modified synthetic polyterpene hydrocarbon resin and Wingtack Registered TM 95, a synthetic polyterpene all having softening points of less than about 100o C. and available from Goodyear Tire and Rubber Co. in Akron, Ohio and Arkon Registered TM P-70, P-90 and P- 100, synthetic petroleum hydrocarbon resins having softening points of 70o C., 90o C. and 100o C. consecutively and available from Arakawa Chemical (U.S.A.) Inc. in Chicago, Ill. Further examples include Hercolite Registered TM 2100 which is a partially hydrogenated cycloaliphatic petroleum hydrocarbon resin available from Hercules, Inc. in Wilmington, Del. and Zonatac Registered TM 105 Lite which is a styrenated terpene hydrocarbon resin, made from d-limonene and available from Arizona Chemical in Panama City, Fla. Useful modified rosins include Sylvatac Registered TM 1103 and Zonester Registered TM 100 available from Arizona Chemical and Permalyn 305 available from Hercules which are all pentaerythritol rosin esters. All of these resins also have softening points of less than about 100o C. Sylvatac Registered TM 1085, an 85o C. softening point glycerol rosin ester of tall oil is another example of a useful rosin based tackifier. It should be noted that there are numerous types of rosins and modified rosins with differing levels of hydrogenation including gum rosins, wood rosins, tall-oil rosins, distilled rosins, dimerized rosins and polymerized rosins. Some specific modified rosins include glycerol and pentaerythritol esters of wood rosins and tall-oil rosins.

Examples of useful pure alphas-methyl styrene resins are Kristalex Registered TM 3070 (70o C. softening point), 3085 (85o C. softening point) and 3100 (100o C. softening point) available from Hercules in Wilmington, Del.

It has been found that a small amount of tackifying resin helps to lower the viscosity, to improve adhesion characteristics and to improve flexibility as measured by Young's Modulus. The lower the Young's Modulus, the more flexible the adhesive. Too much resin results in unacceptable smoke generation. The tackifying resins are useful from 0% to about 10% by weight of the composition, preferably from about 1% to about 10%, more preferably from about 3% to about 7% and most preferably from about 3% to about 5% by weight of the composition.

The tackifying resins found to be preferable to the present invention are those resins which are low in aromatic content and high in saturation, or in other words, are highly hydrogenated having few double bonds. Preferably, these resins are hydrocarbon resin. preferred resins include the Eastotac Registered TM series of hydrocarbon resins and Escorez Registered TM 5300 and 5400 which are hydrogenated cycloaliphatic hydrocarbon resins. It is surmised that these types of resins produce less smoke generation than other types of tackifying resins. In a preferred embodiment of the present invention, 3% by weight of a hydrocarbon tackifying resin is used.

A liquid component or plasticizer may optionally be used in the compositions of the present invention. The most relevant plasticizers are liquid elastomers including polybutenes and polyisobutylenes. These liquid components reduce viscosity and increase flexibility. Examples of useful plasticizers include Parapol Registered TM 1300, a liquid polybutene available from Exxon Chemical Co. in Houston, Tex. and Indopol Registered TM H-50, H-100 and H-300, liquid butene homopolymers available from Amoco Corp. in Chicago, Ill. It is desirable that these liquid components do not increase the tack of the finished composition. They are useful in amounts up to about 10% by weight of the composition.

A stabilizer or antioxidant is also preferably used in hot melt adhesives. These compounds are added to protect the adhesive from degradation caused by reaction with oxygen induced

by such things as heat, light or residual catalyst from the raw materials such as the resin. Such antioxidants are commercially available from Ciba-Geigy in Hawthorne, N.Y. and include Irganox Registered TM 565, 1010 and 1076 which are hindered phenols. These are primary antioxidants which act as radical scavengers and may be used alone or in combination with other antioxidants such as phosphite antioxidants like Irgafos Registered TM 168 available from Ciba-Geigy. Phosphite antioxidants are considered to be secondary antioxidants and are generally not used alone. These are primarily used as peroxide decomposers. Other available antioxidants are Cyanox Registered TM LTDP available from Cytec Industries in Stamford, Conn., and Ethanox Registered TM 1330 available from Albemarle Corp. in Baton Rouge, La. Many such antioxidants are available either to be used alone or in combination with other such antioxidants. These compounds are added to the hot melts in small amounts and have no effect on other physical properties.

Other compounds that could be added that also do not affect physical properties are pigments which add color, fluorescing agents, UV absorbers and odor masks. Of particular importance to the adhesives of the present invention are pigments including titanium dioxide which adds whiteness to a product. This can be important to the aesthetics of a finished article. Additives like these are generally added in small amounts of less than 5% by weight of the composition, more typically even less than about 2% by weight of the composition and are known to those skilled in the art.

These compositions are characterized as having an oxygen index of greater than about 23 and preferably greater than about 25 (atmosphere is 21 and is unacceptable for flame retardance) as measured by Test Method No. 1 for Oxygen Index included in this specification.

They are further characterized as having a smoke number of preferably less than about 6 as measured by Test Method No. 2 included in this specification, more preferably less than about 5 and most preferably less than about 3. It should be noted that this is a qualitative and subjective test which may vary from operator to operator. It is also a relative rating of the examples tested.

They are further characterized as being flexible having a Young's Modulus, as measured by the Tensile and Elongation test found in the Examples Section of the Specification, from about 1500 kg/cm<sup>2</sup> to about 10,500 kg/cm<sup>2</sup> and preferably from about 2500 kg/cm<sup>2</sup> to about 6000 kg/cm<sup>2</sup>.

The compositions of the present invention are light in color having a yellowness index (also b value or yellow-blue index) of less than 5 and preferably from about 1 to about 3 as measured using a Minolta Chromameter, Model No. CR-331 and an L value or black-white index, another important indicator of whiteness of less than 100, preferably from about 75 to about 100 and most preferably from about 90 to about 100.

The viscosities are preferably less than about 30,000 cPs at about 150° C., preferably less than about 25,000 cPs and more preferably less than about 20,000 cPs at 150° C., although the acceptable viscosity will depend on the temperature of application and the equipment used to apply the composition. The temperature of application of a composition containing alumina trihydrate is typically about 135° C. to about 150° C., but may even be 120° C. or less but is generally never higher than about 150° C. because the aluminum trihydrate can begin to release water of hydration at such temperatures. The temperature of application for magnesium hydroxide may be higher. The application temperature is therefore dependent on temperature at which the flame retardant is activated. The viscosity is limited by the application equipment.

The peel values are greater than about 40° C., preferably greater than about 45° C., more preferably greater than about 50° C. and most preferably greater than about 55° C. Peel

values are an indication of the heat resistance that a hot melt adhesive may have, or in other words, may be a measure of the temperature at which an adhesive bond may fail. This is important for shipping and storage when the products may be exposed to higher ambient temperatures. It is important to note that this is not an absolute number, but rather gives an indication, relative to other hot melt adhesives, as to which hot melts have better heat resistance than others.

These compositions are useful in applications where flame retarding characteristics are desired and may be used in the filter industry, for pipe wrapping, as flexible heat duct sealants and for potting and encapsulation of electrical components. Of course, the physical requirements for the compositions will be different depending on the application in which they are used.

These compositions are particularly useful as adhesives for air filters generally and specifically they are very useful for High Efficiency Particulate Air (HEPA) filters. These filters remove airborne contaminants and are used in highly technical manufacturing such as in the medical, chemical, food processing, space, nuclear, semiconductor and computer industries.

HEPA filters are generally pleated to increase filter surface area. This may be accomplished by folding a continuous strip of material back and forth resulting in an accordion-like shape. It is necessary to keep the pleats of the filter separated or spaced apart in a permanent and secure manner for however long the filter may be used which may be accomplished with various types of spacers including adhesives.

The adhesive is generally applied to the material of the filter material or filter media when the filter material is still in a continuous strip and has not yet been folded or pleated, or in other words, prior to folding or pleating the filter material into the accordion-like shape. However, the adhesive may also be applied after pleating. The filter material may also be referred to as the filter media, and for filters requiring flame retardancy, is generally made of a fiber glass composite material.

The adhesive may be applied in a continuous bead or it may be in a discontinuous (intermittent or interrupted) or stitch pattern. In the former case, the filter is pleated after the adhesive is applied but while the adhesive has not yet set and is still warm and ductile. In the latter case, the adhesive is laid down in a pattern such that the adhesive is between the pleats and invisible when looking at the outside of the filter. These filters have a honeycomb type appearance when they are in the final form.

These filters come with differing numbers of pleats and the pleats may have different depths from filter to filter depending on air flow requirements and the performance required of a particular filter. The process of using the adhesive to bond the pleats, therefore supporting and separating them, is also referred to as pleat separation or filter pleating. Different types of HEPA filters are discussed in U.S. Pat. No. 4,365,980 to Culbert et al. issued Dec. 28, 1982, U.S. Pat. No. 4,885,015 to Goulet et al. issued Dec. 5, 1989 and in U.S. Pat. No. 5,098,767 to Linnerston issued Mar. 24, 1992.

The filters are required to pass an Underwriters' Laboratory test, UL 900 TEST PERFORMANCE OF AIR FILTER UNITS. There are two classes of air filters: Class 1 and Class 2. A Class 1 air filter unit shall not produce flame or sparks when subjected to the flame-exposure and spot-flame tests, and during the flame-exposure test shall not cause the development of an area of more than 16.1 cm<sup>2</sup> as measured below the smoke density time curve.

Class 2 air filter units shall not produce flame or extensive (25 or more) sparks which are sustained beyond the discharge end of the test duct when subjected to the flame-exposure test and shall not cause the development of an area of more than 58 cm<sup>2</sup> as measured below the smoke-density time curve.

An adhesive material used for coating the filtering medium or other part of an air filter unit shall have a flash point of not less than 163o C. as determined by the Test Method for Flash and Fire Points by Cleveland Open Cup, ASTM D92-78.

These test methods are available from UL (UL 900).

It is desired that the compositions of the present invention pass Class 2 air filter unit testing. It is also possible to use the compositions on Class 1 air filters if the amount of adhesive is decreased.

The following non-limiting examples further illustrate the invention.

#### Examples 1-8 and Comparative Example A

The adhesives were prepared using a high shear sigma blade mixer such as those manufactured by J.H. Day in Cincinnati, Ohio. The temperature of these mixers is maintained between about 135o C. and about 150o C. The ethylene copolymers are first added to the mixer followed by the flame retardant fillers. The resultant blend is mixed until smooth and homogeneous. The resin, wax and any liquid component are then slowly added to the mixture to prevent phase separation. Any antioxidant used may be added at any point during preparation including at the beginning, or split and added at different stages during mixing. The pigment may be added at the end or also at any other point if one so chooses. This process may be altered depending on the choice and amounts of the ingredients used of which one of skill in the art would understand.

#### Test Methods

##### 1 . Oxygen Index

This test conforms with ASTM D 2863-74 Test for Flammability of Plastics Using the Oxygen Index Method (type D materials). The procedure is used to determine the relative flammability of cast films of coatings, adhesives and sealants using the G.E. Oxygen Index apparatus for measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion.

##### 2. Smoke Generation (Smoke Number)

The Smoke Number is obtained using the same Oxygen Index apparatus as in Test Method 1 above. A 30-40 mil film was burned in a 30% oxygen environment for 1.5 minutes. The smoke generated is then visually observed and was rated on a basis relative to other samples tested. The samples were then ranked on a scale of 0-10 with 0 being no smoke generation and 10 being dense smoke. This is a qualitative and subjective test and it should be understood that this may vary slightly from user to user. The present inventors have rated the examples on a relative scale.

##### 3. Melt Viscosity

The melt viscosities of the hot melt adhesives were determined on a Brookfield Thermosel Viscometer Model RVDVII + using a number 29BS (solid shaft) spindle. The speed is generally about 50 rpms but the speed, as well as the spindle size, may be varied depending on the viscosity.

##### 4. Color

A Minolta Chromameter CR-331 (Colorimeter) was used to measure color. A sample of adhesive was heated in an oven until just molten and is then poured onto release paper making sure that the sample, once cool and set, has no air bubbles. Three values are measured by the instrument: L is the value obtained for lightness, a is the red-green index and b is the yellow-blue index. The L value ranges from 0 (black) to 100 (white), a ranges from + red to - green and b ranges from + yellow to - blue. In this case, the L value and the b value are of importance in determining the whiteness of the sample. For the b value, the more negative the whiter the product or the more positive the yellower the product.

#### 5. Tensile and Elongation, Young's Modulus

Young's Modulus was determined using ASTM D-638. The die used is an ASTM D-638 Type IV die. A one inch gauge with a video extensometer is used to monitor elongation. The strain rate used is 5.08 cm/minute. Young's Modulus is a method of ranking the relative flexibility adhesive films. The film thickness used is 20-30 mils. The resistance to tensile deformation is measured at small strains. All samples were tested at about 23o C. (room temperature).

#### 6. Programmed Oven Peels

Peel and/or shear values were determined by placing samples in a programmed oven with 100 g weights for the peel mode and 500 g weights for the shear mode, and ramping the temperature up from about 25o C. to 125o C. at 25o C./hour. The oven automatically recorded the temperature at which the samples failed. Each sample was coated onto kraft paper by hand using glass rods or shims. A top sheet of kraft paper is rolled down onto the bottom sheet of kraft paper onto which the hot melt is poured. The rods are then used to roll the adhesive down as well as for mating the top sheet of kraft to the bottom sheet. Release paper is used on either side of a 2.54 cm strip on the bottom sheet of kraft paper. The resultant coating is then a one inch wide band that is about 8-10 mils or about 0.02 cm to about 0.03 cm thick. Four to five bonds were made for the peel mode and four to five bonds were made for the shear mode and the results were averaged.

TABLE I

Examples	1	2	3	4	5	6	7	8	9	A
EVA (28-400)	-	-	-	-	-	-	-	-	-	25.5
EVA (28-800)	33.5	33.5	20.5	20.5	20.5	30	20	20	33.5	-
EVA (28-2500)	-	-	15	15	15	30	-	15	-	-
Parapol										
Registered TM										
1300 polybutene	-	-	-	-	3	-	-	-	-	-
Escorez										
Registered TM										
2596										
hydrocarbon	-	-	-	-	-	-	-	-	-	26.5
resin										
Escorez										
Registered TM										
5400 hydrocarbon	-	7	3	3	-	-	10	-	-	-
resin										
Paraflint										
Registered TM H-										
4	20	13	15	15	15	10	25	15	-	9
synthetic HMP										
wax										

Microcrystalline Wax 1950 F.	-	-	-	-	-	-	-	-	20	20.0
Alumina Trihydrate 8 microns	-	-	-	-	-	-	-	-	-	37.5
Alumina Trihydrate 6 microns	-	-	-	-	35	-	-	-	-	-
Alumina Trihydrate 5 microns	25	25	25	35	-	28.5	43.5	10	25	-
Alumina Trihydrate 4 microns	-	-	10	10	-	-	-	-	-	-
Firebrake ZB zinc borate	20	20	10	-	10	-	-	38.5	20	-
Titanium Dioxide white pigment	1	1	1	1	1	1	1	1	1	1
Viscosity @ 135o C.	11920	16520	12320	12100	10900	18240	2220	13340	19600	9540
Viscosity @ 149o C.	8300	11380	8280	8500	7480	12420	1550	9320	13480	-
Oxygen Index	25.5	24.5	25.5	26.5	25.0	23.5	27.0	24.5	25.5	25.5
Smoke Number	2	6	2	3	3	5	6	2	2	8
Young's Modulus	8230	3060	5520	4695	4065	1960	10210	5685	3910	3460
Color (L value)	93.81	94.70	93.61	93.63	93.92	95.39	94.26	95.70	95.14	92.98
Color (B value)	1.60	1.85	3.00	3.10	2.45	2.60	3.10	1.15	3.45	4.75

Example 1 illustrates a composition which is mid-range for all ingredients and having no tackifying resin.

Example 2 illustrates a composition which has a relatively higher tackifying resin content than the other examples tested. The smoke generation is increased and is higher than what is preferable to the present invention but is still acceptable.

Example 3 illustrates a medium range composition for ingredients but has less tackifying resin than Example 2 and also has less smoke generation.

Example 4 has the same ingredients as Example 3 but has only a hydrated inorganic flame retardant. A higher oxygen index and a slightly higher smoke number were obtained.

Example 5 illustrates a composition using a maximum amount of flame retardant and no tackifying resin. The flame retardant characteristics are not improved in this instance. The Parapol Registered TM 1300 liquid polybutene is used to improve flexibility in this case.

Example 6 illustrates the maximum amount of ethylene vinyl acetate which may be employed



while still retaining an acceptable viscosity profile for the finished product, and also represents a sample having a minimum amount of hydrated inorganic flame retardant. The oxygen index is at the lower end of what is acceptable and the viscosity is on the higher end, although this product is still within an acceptable range to the present invention.

Example 7 illustrates the maximum amount of resin desirable and the smoke number is greater than what would be preferred in the present invention.

Example 8 illustrates the maximum amount of the zinc borate flame retardant which is desirable. The oxygen index is slightly below that which is preferred in the present invention, although it is acceptable.

Comparative Example A illustrates a composition having a resin content which is too high resulting in a high smoke number, 8, indicating that the smoke generation is unacceptable for the present invention.

**CLAIMS:** We claim:

**[\*1]** 1. A High Efficiency Particulate Air Filter comprising:

- a) a material effective for filtering airborne contaminants; and
  - b) a hot melt adhesive applied to said material said adhesive comprising:
    - i) about 10% to about 60% by weight of the adhesive of at least one copolymer of ethylene;
    - ii) about 10% to about 50% by weight of the adhesive of a hydrated inorganic flame retarding compound; and
    - iii) about 5% to about 30% by weight of at least one high melting point wax; and
- 0% to about 10% by weight of at least one tackifying resin

wherein said filter is pleated after application of said adhesive to said material.

**[\*2]** 2. The filter of claim 1 wherein said hot melt adhesive is applied in a pattern selected from the group consisting of continuous and stitched.

**[\*3]** 3. The filter of claim 1 wherein said filter material is made of a fiber glass composite material.

**[\*4]** 4. The filter of claim 1 wherein said hydrated inorganic compound is selected from the group consisting of alumina trihydrate, magnesium hydroxide and mixtures thereof.

**[\*5]** 5. The filter of claim 1 wherein said hot melt adhesive further comprises up to about 40% by weight of the composition of zinc borate.

**[\*6]** 6. The filter of claim 1 wherein said hot melt adhesive has an oxygen index of greater than about 23.

**[\*7]** 7. The filter of claim 1 wherein said hot melt adhesive has an oxygen index of greater than about 25.

**[\*8]** 8. The filter of claim 1 wherein said hot melt adhesive has a smoke number of less than about 5.

**[\*9]** 9. The filter of claim 1 wherein said hot melt adhesive has a yellow-blue index from about 0 to about 5 and a black-white index from about 75 to about 100.

**[\*10]** 10. The filter of claim 1 formed by a method comprising the steps of:

- a) applying said adhesive to said filtering material said filtering material being in a strip and in an unpleated state; and
- b) pleating the filter material by folding it back and forth until it is in an accordion-like shape while said hot melt adhesive remains ductile.

**[\*11]** 11. A High Efficiency Particulate Air Filter comprising:

- a) a material effective for filtering airborne contaminants; and
- b) a hot melt adhesive applied to said material said adhesive consisting essentially of:
  - i) about 10% to about 60% by weight of the adhesive of at least one copolymer of ethylene;
  - ii) about 10% to about 50% by weight of the adhesive of a hydrated inorganic flame retarding compound; and
  - iii) about 5% to about 30% by weight of at least one high melting point wax; and
  - iv) 0% to about 10% by weight of at least one tackifying resin

wherein said filter is pleated after application of said adhesive to said material.

Source: [All Sources](#) : [Patent Law](#) : [Patents](#) : [U.S. Patents](#) : [Utility Patents](#) 

Terms: **"phosphate ester" w/s fluoropolymer** ([Edit Search](#))

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